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ARTIFICIAL SILK

A COMPREHENSIVE WORK DEALING WITH
THE MANUFACTURE OF ARTIFICIAL SILK,
FROM THE MAKING OF THE RAW MATERIAL
TO THE FINISHING AND AFTER TREATMENT
OF THE FINAL PRODUCT

BY
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Translated from the German by
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TRANSLATOR'S PREFACE

THE Artificial Silk Industry has now reached a stage of development at which increasing attention is necessarily directed to the scientific study of the processes on which it is based, for example, on the chemical and physical characteristics of spinning solution and fibre, and the chemistry and physics of the spinning process itself. Success or failure obviously depends very largely on the perfection and regularity with which the last-named very delicate and complicated process is carried out.

The tendency to increased study of such matters is reflected in the present volume by Dr. O. Faust, in which much space is devoted, for example, to the structure of cellulose and of artificial silk fibres, as revealed by X-ray analysis and other methods, to the study of swelling-power, the character of the spinning process—and more particularly of the stretch-spinning process—and the ripening of viscose.

After an historical introduction, the author devotes approximately one-half of the volume to a discussion of the chemical and physical properties of spinning solution and fibres and the methods of their scientific investigation. In the subsequent technical section he then describes the raw materials of the industry, spinning processes and apparatus, after-treatment processes and the manufacture of nitrate, acetate, cellulose ether, cuprammonium, and viscose silk. The volume is completed by a chapter on statistics and by a bibliography.

The translator has endeavoured to reproduce the author's meaning and opinions as faithfully as possible, with the object of making Dr. Faust's valuable contribution to the subject more readily available to English-speaking readers.

ERNEST FYLEMAN

SUTTON, SURREY,

January, 1929.

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ARTIFICIAL SILK

HISTORICAL INTRODUCTION

THE idea of imitating the fine, smooth, endless thread of the silkworm by artificial means was suggested by Réaumur in 1734, who proposed the use of solutions of gum and so forth as raw materials. Hitherto, it has been generally supposed that Réaumur was the first to make this suggestion. Latterly, however, his position in the matter has been disputed in favour of the Englishman, Robert Hooke,¹ who was born at Freshwater, Isle of Wight, on the 18th July, 1635, and died in London on the 3rd March, 1703. A scientific treatise on his *Microscopic Observations of Natural Objects* was published by the Royal Society of London in 1665. In this treatise he describes, amongst other matters, very fine silken fabrics and a fabric of artificial dyed material of horn or isinglass, transparent and gum-like, which softened in water. He mentions, in this connection, that he had often thought that a process might be found of manufacturing an artificial gummy mass which would behave as well or even better than the spinning material of the silkworm. He suggests that a process of spinning such a mass into threads could certainly be easily and quickly found. Since that date the endeavour to produce artificial threads from albuminous materials has never definitely ceased; in these endeavours the main idea was probably that the strength when dry, and resistance to water, of a thread produced from such material, and also its dyeing properties, would closely resemble those of natural silk.

The only product of this nature which was for a short time an article of commerce was A. Millar's "Vandura Silk," produced according to German patent 88,225, but even this

* See Dr. Martin W. Neufeld, *Die Kunstseide*, 9, 268, (1927).

was unable to maintain its position, owing to its great sensitive-ness to water. Other attempts to use casein and albumen as raw materials have led to a few patent applications, but have never reached the stage of practical application.*

Cellulose is the only raw material from which artificial silk has successfully been manufactured by various methods. It is the raw material which has to serve to-day for the enormously expanded artificial silk industry of the whole world, and if one considers that the present world's production exceeds 100,000 tons annually, one may form some idea of the difficulties which would have to be overcome if some material other than cellulose, which is available in such large quantities in the form of wood, had to be used to satisfy the requirements of the artificial silk industry.

The Frenchman, Audemars, was the first to use as a raw material a solution in ether-alcohol of cellulose nitrate, which had been discovered by Schönbein. He obtained in England the first artificial silk patent granted in the world; † but experience—more particularly technical experience—of cellulose nitrate was at that time so slight that his experiments did not lead to success. Much later, in 1897, the solution of cellulose in ammoniacal copper solutions, discovered in 1857 by Schweizer, was successfully used by Fremery and Urban for the manufacture of artificial silk (German patent 98,642 (Pauly)). ‡ Attempts were also made to produce artificial threads from finely-spun glass. The first, however, who really succeeded, after working for decades, in producing artificial silk on a technical scale, was Count Hilaire de Chardonnet, who obtained a patent for artificial silk from cellulose nitrate in 1884.

The manufacture of cellulose nitrate silk flourished in France and Belgium. In Belgium before the war, 3000 kg. were produced daily, which was a considerable output in those days. In Germany a very good artificial silk from cellulose nitrate was also produced in the artificial silk works at Jülich. In

* See the Summary of F. Reinthaler, *Die Seide*, 32, 134–137 (1927).

† Audemars, British patent 283/1855.

‡ Hottenroth, *Artificial Silk* (Pitman).

Germany this manufacture has almost ceased on account of the very high cost of alcohol and ether, although processes for the recovery of these materials had been greatly perfected during the war (see pages 89-92) and are now available for this purpose, more particularly the charcoal absorption process of Farbenfabriken vorm. Bayer & Co., Leverkusen. The older process of absorption by sulphuric acid enabled large sums and large quantities of material to be saved during the war, more particularly in connection with the manufacture of smokeless powder.

Apart from cellulose nitrate silk, cuprammonium silk was more particularly produced in Germany by the Erste Glanzstoffabrik, Oberbruch nr. Aachen. This process was later developed very greatly by J. P. Bemberg, A.G. The manufacture of artificial silk expanded enormously, when the production of cellulose xanthate, discovered in 1892 by Cross, Bevan and Beadle, was successfully used for artificial silk manufacture. Attempts to utilize this reaction were not lacking immediately after its discovery, but the problem was only solved with the help of the fundamentally new German patents for precipitating baths, owned by the Vereinigten Glanzstoffabriken, Elberfeld.

A process which is to some extent analogous to the manufacture of cellulose nitrate silk is the manufacture of cellulose acetate silk, which has only been developed extensively since the war, and also makes use of organic solvents; and finally, we may mention Lilienfeld's cellulose-ether silk, which has not yet been manufactured on a technical scale.

With regard to the development of the artificial silk industry during the last 25 years, we refer the reader especially to the description by Dr. Conrad Claessen in the Jubilee Number of the *Papierfabrikant*.*

* Conrad Claessen, "Twenty-five Years of Artificial Silk," Jubilee Number of the *Papierfabrikant*, 102 (1927). See also H. Kaiser, *Die Seide*, 23, 3 (1928).

PART I. GENERAL SECTION

CHAPTER I

CELLULOSE

Introduction. We have mentioned that cellulose is to-day the only raw material which can be used for the artificial silk industry, now that the problem of dissolving this material, which appears to be chemically so resistant, has been solved by the various methods which have just been referred to. According to the results of the latest X-ray investigations, which have been carried out more particularly by Debye and Scherrer, by O. Herzog and by J. R. Katz, natural cellulose in the form of cotton, linen, flax, jute, ramie and wood pulp has a regular crystalline structure. It is hardly possible to dissolve cellulose without chemical change. The formation of an ether or an ester is almost always required, and even the cuprammonium solution must be considered to contain a chemical compound. We must here refer more particularly to the very comprehensive work of W. Traube on the action of cuprammonium and of compounds of organic amines (more particularly of 1-2 diamines) on glycerine and other poly-hydroxlic compounds of known constitution.

Analogous compounds of cellulose are only conceivable after partial or complete dissociation of the internal anhydride formation of the native cellulose, which is assumed by some investigators.

The only method which possibly enables cellulose to be dissolved without chemical change is that which was first described by P. P. von Weimarn (German patent 275,882/1912), namely, the treatment of cellulose with strongly hydrolyzing, concentrated salt solutions, such as solutions of calcium sulphocyanide, lithium chloride and similar compounds. These comprehensive investigations of von Weimarn were to some extent anticipated by others. Thus Wynne and Powell

(British patent 16,805/1884) discovered the solubility of cellulose in zinc chloride, and Dubosc prepared solutions of wood pulp in ammonium sulphocyanide and calcium sulphocyanide solutions.

This solubility, which is disputed by Cross and Bevan, as also the solubility in zinc chloride and in the salt solutions used by von Weimarn, is considerably facilitated by first mercerizing the cellulose or wood pulp to be dissolved. The solutions in zinc chloride solution, which are always acid, very soon change under the hydrolyzing influence of the acid. This is the case to a much greater extent with the well-known solutions of cellulose in concentrated mineral acids, such as 72 per cent sulphuric acid or 40 per cent hydrochloric acid (Willstätter, German patent 273,800).^{*} The last-named process has hitherto attained no importance in the artificial silk industry, and is more applicable to work on the saccharification of cellulose.

Recently, the Badische Anilin und Sodafabrik (German patent 408,821) has described a process for the manufacture of cellulose solutions, according to which cellulose is treated with chloral in the presence of tertiary organic bases, such, for example, as quinoline. In this manner a solution is obtainable which is stable for some months, although not permanently so; it is, however, difficult to regenerate cellulose from these solutions.

All technical solutions of cellulose and cellulose compounds are of colloidal character. In these solutions the cellulose is usually hydrophil, and the dissolved substances, even in small concentrations, increase the viscosity of the solvent to a very considerable degree. In dealing with cellulose compounds, such as the nitric acid esters of cellulose, wrongly known as "nitro-cellulose" or the acetic acid esters of cellulose, volatile organic solvents such as mixtures of ether and alcohol, acetone, mixtures of alcohol and benzene are used, or chloroform and similar chlorinated substances for dissolving the acetic esters. (For details, see the later sections dealing with this subject.) The solutions so obtained, when poured on to glass plates,

^{*}Willstätter and Zechmeister, *Ber.*, 46, 2403 (1913).

leave the cellulose ester as a completely reversible colloid in the form of a more or less transparent film after evaporation of the solvent.

In the case of the aqueous or alkaline solutions of cellulose xanthate, which is to be considered, according to the investigations of its discoverers, Cross and Bevan, as the sodium salt of the acid cellulose ester of dithiocarbonic acid, it is also possible to precipitate the xanthate in a reversible condition by means of certain precipitants, such as concentrated sodium chloride solution, methyl and ethyl alcohols, and so forth, but the precipitated jelly, which still contains much water, is very unstable and decomposes continuously. The cuprammonium solution of cellulose is precipitated irreversibly by fixation of the ammonia with an acid or by displacing the ammonia by sodium hydroxide solution; in the first case, insoluble cellulose hydrate is precipitated, and in the latter case, copper alkali cellulose.

The esterification of cellulose, or its solution in concentrated salt solutions or in cuprammonium solution, is always attended by a more or less deep-seated chemical alteration of the cellulose complex. The cellulose regenerated from cellulose solutions is generally known as cellulose hydrate, and its colloid-chemical properties differ greatly from those of the initial material. A chemical proof of the hydration of this regenerated cellulose has not so far been carried out; on the contrary, it is chemically identical with native cellulose,* but the colloid-chemical characters, more particularly the more or less marked capacity for gelatinizing, are looked upon as a proof of its hydration; for this reason, C. G. Schwalbe† proposes the much more satisfactory name of "gelatinizable cellulose." We may here mention that both cuprammonium cellulose solutions, and also cellulose xanthate and its solutions in water or alkali hydroxide solution, absorb oxygen freely. Alkaline copper-cellulose solutions, and also the sodium trithiocarbonate which always accompanies cellulose xanthate, show the same property. A sodium

* Ost and Westhoff, *Chem. Ztg.*, 33, 197 (1909); *Liebig's Ann.*, 382, 354 (1911).

† *Ullmann's Enzyklop. d. techn. Chemie*, 3, 333 (1916), article on "Cellulose."

trithiocarbonate solution of a given strength absorbs oxygen at the same rate as the cellulose xanthate solution of corresponding strength.

It must, however, be assumed that in the latter case the cellulose of the xanthate is also attacked, as a sodium cellulose xanthate solution which has been prepared in the absence of air regularly shows considerably higher viscosity than a solution similarly prepared with access of air. Alkali cellulose prepared by mercerizing cellulose, for example, in 18 per cent sodium hydroxide solution, also absorbs considerable quantities of oxygen at a considerable rate. It is probable that cellulose solutions in concentrated salt solutions absorb oxygen in a similar manner, and possibly the p_H value plays an important part in this phenomenon.

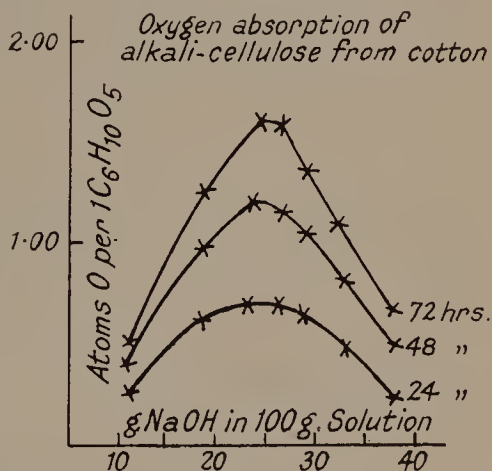


FIG. 1

W. Weltzien and G. zum Tobel* have investigated experimentally the process of oxidation of alkali cellulose from cotton, and also of cellulose hydrate obtained in fibrous form from cuprammonium cellulose solutions, by atmospheric oxygen, a phenomenon which is well-known to practical workers.† The so-called gelatinization alkali‡ can be calculated by determination of the total alkali with the help of Vieweg's§ assumption that in a liquid containing 16 per cent and more of NaOH, 0.5 molecules of alkali combine with 1 molecule of C₆H₁₀O₅. The dependence of the rate of absorption of oxygen and the absorbed amount on the concentration of the alkali solution will be seen from the appended curves (Fig. 1) for cotton alkali cellulose. In the case of alkali

* *Ber.*, 60, 2024 (1927); *Die Seide*, 32, 371, 414 (1927).

† C. G. Schwalbe, *Chemie der Zellulose* (Borngräber, Berlin, 1911), p. 50.

‡ W. Weltzien and G. zum Tobel, *Seide*, 31, 132 (1926).

§ *Ber.*, 57, 1917 (1924); *Zts. f. angew. Chem.*, 37, 1008 (1924).

cellulose from wood pulp, the rate of absorption of oxygen is still greater.

The quantities of oxygen absorbed by alkali-cellulose and determined by the above-mentioned investigators are therefore considerable. This absorption is attended by neutralization of alkali, on account of which oxidation with formation of acids is assumed. In similar processes Schwalbe suggests the formation of oxy-cellulose.

In an atmosphere of nitrogen, Weltzien and zum Tobel found that no acid degradation products were obtained, but that the solubility in alkali was increased. The action of alkali on cellulose in an atmosphere of nitrogen differs, therefore, completely from its action in presence of air.

It is now, and has for some time, been assumed that in natural cellulose the hydroxyl groups have interacted to form ethers or inner anhydrides, and that consequently natural cellulose does not show the property of swelling, whereas hydrolysis has occurred in the regenerated material known as cellulose hydrate, the alcoholic nature of which then becomes apparent.*

It is still uncertain which view is correct: factors of colloid-chemical character, more particularly the degree of absorption, the size of particle of the regenerated cellulose compared with that of the natural original cellulose, together with the disintegrated crystalline structure, may also be responsible for this phenomenon of gelatinization which is so inconvenient in practice. (See also the section on the "Ripening of Viscose," page 162). In the case of cellulose nitrate, we have a material completely inert to water, in spite of the loss of crystalline structure; but with the exception of the primary triacetyl cellulose, which is of no technical utility, the analogous acetyl celluloses swell appreciably in water.†

Also, if the whole of the three hydroxyl groups of cellulose are not nitrated, that is, if the nitrogen contents are much below 13 per cent, the product no longer swells in water.

* See P. Karrer, *Polymere Kohlehydrate*, pp. 217-240 (Leipzig, 1925, Akadem. Verlagsges.).

† See the section on "Acetyl Cellulose Silk."

The cellulose nitrate used for artificial silk manufacture contains between 10 and 11 per cent of nitrogen and does not swell at all. The conditions are not analogous in the case of acetyl cellulose, although the capacity of acetyl cellulose for swelling is less than that of the so-called cellulose hydrate. Cellulose nitrate, which, as is well known, must be denitrated as a final operation in artificial silk manufacture, on account of its dangerous explosive properties, yields a cellulose hydrate during this treatment which differs in no way from cellulose hydrates regenerated from other cellulose solutions with regard to its capacity for swelling. (See section on "Investigation of Swelling, page 57.)

With the exception of solutions in concentrated salt solutions and possibly also in acids, all treatments technically applied to cellulose, for the purpose of bringing it into solution, are characterized by being chemical processes carried out with a colloidal material; in all cases a more or less deep-seated dissociation of the original micella simultaneously occurs. In consequence, the phenomena are very varied and difficult to classify; but the investigations of Vieweg* on the formation of alkali cellulose during mercerization clearly indicate that chemical reaction occurs in stoichiometric proportions.† Moreover, the extremely interesting work of R. O. Herzog,‡ I. R. Katz and H. Mark,§ I. R. Katz and W. Vieweg,|| and I. R. Katz and K. Hess¶ on the alteration of the X-ray spectrum of cellulose by mercerization, indicate a change in the micro-structure of cellulose, which may possibly be due to a loosening of the micro-crystalline structure of the natural cellulose fibre, more particularly during mercerization without tension; ** this may possibly explain the greater reactivity and more powerful dyeing properties of mercerized cellulose compared with those of the unmercerized fibre. We may also refer

* *Ber.*, 40, 3879 (1907); 57, 1917 (1924); *Zts. f. angew. Chem.*, 37, 1008 (1924).

† See also I. R. Katz, *Zellulosechemie*, 6, 35 (1925).

‡ *Naturw.*, 12, 957 (1924).

§ *Zts. f. Elektrochem.*, 31, 112 (1925).

|| *Zts. f. Elektrochem.*, 31, 159 (1925).

¶ *Zts. f. physik. Chem.*, 122, 126 (1926).

** I. R. Katz, *Zts. f. physik. Chem.*, 124, 352 (1927).

found the heat of combustion of cellulose to be 4185 cal. The dissociation of the micellae by mercerization, or solution of a cellulose ester, or by regenerating the cellulose after solution as ester is not, therefore, accompanied by an alteration in the energy content of the material, within the experimental error; this may be explained by the small energy inherent in the space lattice of polysaccharide molecules. (See also W. Biltz.*) The alteration from the crystalline condition in sulphite pulp, compared with the mainly amorphous condition in the regenerated cellulose, appears to entail no essential change in the energy content of the material.†

This more or less considerable dissociation of the original micella is considered by the author to be the reason for the varying degrees of viscosity‡ which are obtained with one and the same raw material, after varying pre-treatment and subsequent solution by any of the known processes.§ Cellulose may be pre-treated with acid|| or may be mercerized with 18 per cent sodium hydroxide solution, and the pressed and suitably disintegrated mass may be allowed to ripen for a varying length of time; other methods of treatment are also known, for example, the pre-treatment proposed by Linkmeyer for the preparation of viscose, consisting in the action of dilute or concentrated mineral acids, by which means it is possible to diminish the viscosity of the solution subsequently obtained. According to Reitstötter,¶ the viscosity of the cellulose nitrate solution or cuprammonium cellulose solution ultimately obtained may be considerably diminished by previously heating the cellulose or wood pulp *in vacuo* to temperatures, for example, of 90° and 140° C. Reitstötter established the fact, which is highly interesting for artificial silk laboratories,

* Zsigmondy-Festschrift (*Kolloid-Zts.*, 36, 49 (1925)).

† According to M. Bergmann (see p. 13) it is possible that in the case of carbohydrates of high molecular weight, in an amorphous condition, the various degrees of aggregation occur simultaneously.

‡ See also Ost and Westhoff, *Liebig's Ann.*, 382, 340 (1911).

§ Prof. H. Mark has very kindly pointed out to the author that the degree of adsorption of the solvent by the dissolved substance also influences the viscosity.

|| R. Linkmeyer, German patents 337,672, 344,749, and 394,436, all of 1919; see also German patent 363,715 of Zellstoffabrik Waldhof and V. Hottenroth.

¶ J. Reitstötter, *Kolloid-Zts.*, 41, 362 (1927).

that the viscosities of solutions of cellulose nitrate and cuprammonium cellulose solutions obtained from celluloses treated in this manner, are in the same ratio as the viscosities of solutions obtained from celluloses which have not been thus pre-heated. Such methods of pre-treatment are used in all industries which convert cellulose into solutions, whether for the manufacture of cellulose nitrate varnish* or for the manufacture of viscose solutions, and so forth.

By means of the carefully regulated application of these methods of treatment, it is possible always to obtain a uniform viscosity in the cellulose solutions, on a manufacturing scale, whilst allowing certain variations in the raw material. This requirement is of extreme importance, and is probably one of the main reasons why, formerly, cotton of the same origin was always used for the manufacture of spinning solutions, which ensured great uniformity of its chemical properties. In the viscose process, however, the manufacturers soon turned to the use of sulphite pulp, as in this process an excellent means existed, in the form of the ripening process, for equalizing the very variable viscosities which would otherwise occur with various batches of wood pulp, even from the same works. It must, however, be emphasized that in technical practice all pre-treatments of pulps and celluloses cause a reduction—never an increase—of the viscosity, with the exception of the production of viscose *in vacuo* (page 7), which merely excludes the action of the atmospheric oxygen, which lowers the viscosity and partly changes the chemical nature of the

* After-treatments for the reduction of the viscosity are also known; for example, the after-treatment of cellulose nitrate before solution; see for example, E. von Müllendahl and J. Reitstötter, *Umschau*, 31, 244 (1927); see also J. Scheiber, *Lacke und Ihre Rohstoffe*, p. 101 (J. A. Barth, Leipzig, 1926). In this connection a fact is of interest which was discovered by H. Pringsheim, who applied for patents for the process some considerable time ago, and which he mentioned at a meeting of the Association of Paper and Pulp Chemists in Berlin in 1927—namely, that acetyl-cellulose compounds undergo perfectly definite and reproducible reductions in their viscosity by heating to definite temperatures, for example, in boiling toluene; Pringsheim considers this phenomenon to indicate a dissociation of the cellulose molecule (see also the corresponding publications on the dispersion of the polyamyloses, by H. Pringsheim and P. Meyersohn, *Ber.*, 60, 1709 (1927); see also E. Kasten, Dissertation, Berlin, 1927. The viscosities of cellulose nitrates of equal nitrogen contents depend on the contents of H_2SO_4 in the nitration acid; see E. Berl and E. Berkenfeld, *Zts. f. angew. Chemie*, 41, 130 (1928).

solution.* Wood pulps which show too low a viscosity have been too strongly degraded or depolymerized, a fault which cannot at present be corrected in technical practice.

In this connection it is of interest to refer briefly to the interesting views expressed by Max Bergmann on the structure of materials of high molecular weight.†

Bergmann describes each aggregate of directly combined atoms, the combination of which is unaffected by the reversible change from one state of aggregation to another, as the individual group. As Bergmann has shown in the case of inulin, even with substances of high molecular weight we are often merely dealing with a reversible aggregation or association of two, or sometimes more, individual groups. All the structural phases which may be reversibly converted one into another by changes of temperature and pressure, or by the addition or removal of solvents, can be grouped into one material system. In this case, however, in analogy to the views of A. Werner, the chemical structural formula of such materials, for example, in the dissolved and in the solid condition, or dissolved in two different solvents, need in no way be the same, but may differ in the manner which has already been assumed in the case of substances which, for example, change their colour on being converted from the one to the other condition. The gaseous and the crystalline conditions are in this case to be considered as two essentially different conditions of valency and structure. Bergmann thinks it probable that, apart from the crystalline condition, various degrees of aggregation occur simultaneously. According to I. R. Katz,‡ the size of the molecule or degree of polymerization cannot be determined with certainty from the X-ray diagram, even in the case of crystalline substances, or in the case of amorphous materials such as rubber and isoprene.

Staudinger, Johner, Ligner, Mie and Hengstenberg§ came

* See K. Hess, *Ann.*, 435, 120 (1923); 455, 180 and 186 (1927); *Naturw.*, 12, 1152 (1924); *Zts. f. Elektrochemie*, 31, 318 (1925).

† See M. Bergmann, *Ber.*, 59, 2973 (1926); *Kolloid-Zts.*, 40, 289 (1926); *Naturw.*, 14, 1224 (1926); *Liebig's Ann.*, 452, 12 (1927); *Gerber*, 52, 195 (1926).

‡ I. R. Katz, *Zts. f. physik. Chem.*, 125, 321 (1927).

§ H. Staudinger, H. Johner, K. Ligner, G. Mie and J. Hengstenberg, *Zts. f. physik. Chem.*, 126, 425 (1927); and H. Staudinger, H. Johner, M. Lüttig, and R. Singer, *Naturw.*, 15, 379 (1927).

to the same conclusion when investigating crystalline, highly-polymerized polyoxymethylenes, which they thought might be considered as models of the cellulose molecule. With the fruitful assistance of X-ray analysis, the magnitude of the elementary crystal may be determined, but it is not yet certain whether this elementary body may not under certain conditions be smaller than the individual molecule, which latter is identical with Bergmann's individual group.

The many analogies in the behaviour of india-rubber and cellulose may be considered as a constant source of stimulus for investigators. (See, for example, the papers* at the First General Meeting of the German India-rubber Society.) The dissolution of chemical bonds within an individual group only occurs with irreversible change of the individual character of the substance characterized by this group. In the case of substances of "pseudo high molecular weight," very strong aggregation or association of individual groups occurs, caused by strong forces which act beyond the molecular groups. In contrast with this condition, a substance *A* and its polymerized product *B* represent two different substances, different in all degrees of aggregation and in all derivatives, which cannot become identical by equalization of temperature, pressure or solvent, so long as their material properties remain unaltered.

In the case of the higher carbohydrates, Bergmann suspects a somewhat indefinite difference between the behaviour of the bonds uniting the aggregates, which are very stable, and those of the individual aggregates.† He considers it possible that if derivatives are produced with care—for example, by acetylation—only reversibly dissociable aggregating bonds are dissociated. In the case of inulin it was possible to confirm this view. Solid inulin, its colloidal particles in aqueous solution, and its highly dispersed solutions in liquid ammonia, merely represent various states of aggregation of one and the same substance. Whether, on the other hand, in the case of cellulose, the numerous particles which occur in colloidal solution

* R. Punmerer, H. Miedel, I. R. Katz, H. Staudinger, *Zts. f. angew. Chem. Referat*, 40, 757 (1927).

† See also K. Freudenberg's discussion of the formula of cellulose (*Liebig's Ann.*, 1928).

represent the ultimate structural units, or whether they are divisible into still smaller individual groups, is a question which, according to K. Hess,* might probably be answered in the sense of further divisibility, if one may accept the rotatory power of a substance to polarized light, which was investigated by Hess and Schulze, as a definite characteristic.

Doubts on this matter have been lately expressed by E. Hägglund and F. W. Klingstedt.† They point out that according to M. Lüdtke,‡ mannan, from earth nuts, yields dextro-rotatory complex copper compounds, and that according to their own investigation xylan is more strongly laevo-rotatory than cellulose is dextro-rotatory, so that possibly mixtures of mannan and xylan might show the same rotatory power as cellulose, and in this case no conclusion could be arrived at with regard to the purity of the cellulose under investigation from the rotatory power alone. Although this argument cannot be disputed, it would be necessary first to prove that such an unfortunate mixture was present in the investigations of Hess. However this may be, such depolymerization is not desired by the artificial silk manufacturer, as it is not possible to obtain useful fibres of sufficient fineness from such solutions, on account of their low viscosity, and even when this is still possible, there is no method known which enables one to reproduce the original degree of aggregation on precipitation of the fibre, and brittle and weak threads are obtained. It is uncertain whether the higher degree of aggregation may not be caused by high tension and pressure conditions under which the native cellulose fibre is produced (condensed arrangement of the particles and high specific gravity) under the influence of which special forms of aggregation may occur, which are not reproduced on precipitating the dissociated solution in consequence of the absence of these forces. According to my own experience, an orientation and aggregation by means of electric or magnetic fields of force is not possible.

An admixture with celluloses of higher viscosity can only

* K. Hess, *Liebig's Ann.*, 444, 287 (1925); K. Hess and G. Schulze, *Liebig's Ann.*, 448, 99 (1926).

† *Liebig's Ann.*, 459, 26 (1927).

‡ *Liebig's Ann.*, 456, 201 (1927).



be carried out with the greatest care, and only in cases in which the material of lower viscosity is of such a character that it can itself alone be converted into a fibrous product of satisfactory mechanical strength and other properties. For this reason the purely chemical methods of treatment, among which bleaching—which also lowers the viscosity—must be included, must be used with the greatest care and experience.

The large wood pulp producers have now improved the manufacture and after-treatment of wood pulp to such an extent that sulphite pulp of suitable quality can be used for most purposes, not only for viscose silk, but also for cellulose nitrate silk, and partially even for cuprammonium cellulose solutions, for example, in the form of the finest tissue paper for cellulose nitrate. A wood pulp which has not been thoroughly purified* may lead to the greatest difficulties, more particularly in the case of cuprammonium silk and viscose silk, as in this case many gelatinized fibres are present in the spinning solution, which make it impossible to filter the solution. Satisfactory filtration is, however, a necessary condition for the steady operation of the spinning process. The special brands of pulp for artificial silk manufacture which are produced by the large German pulp works generally comply with the necessary requirements; in this connection the Zellstoffabrik Waldhof may be specially mentioned.

Fig. 2 shows such swollen fibres, which have the appearance of a row of pearls, and which float in the spinning solution in a form which is often hardly visible under the microscope. These swollen fibres are more easily visible under the microscope between crossed nicol prisms.

* See the interesting suggestions of G. Tammann and R. Tampke, *Zts. f. anorg. Chem.*, 162, 1 (1927); see also footnote, p. 19.

CHAPTER II

THE SPINNING SOLUTION

The Thread-forming Qualities and the Viscosity. All processes for the manufacture of artificial fibres, including artificial silk, have the common characteristic that the raw material—that is, cellulose—must in some way, by more or less drastic chemical and colloid-chemical change, be converted into a solution, and that this solution, after pre-treatment suitable for the purpose, must be expelled through more or less fine apertures, by which means the required production of an endless fibre is achieved. It is to be expected that the viscous spinning solution should entrain considerable quantities of air bubbles of all sizes, in consequence of the stirring which takes place during its preparation, in so far as this is not carried out *in vacuo*. These bubbles must be removed, particularly if the solution is to be spun through very fine apertures, as the larger bubbles, more particularly, would be driven into the apertures and would cause rupture of the individual threads. The removal of these air bubbles is effected in the case of cuprammonium and viscose solutions by strong and, if necessary, repeated exposure of the mass to a vacuum whilst in as thin as possible a layer, for example, in horizontal and slowly rotating containers which are only one-quarter full. In the case of cuprammonium cellulose solutions, the viscosity of the solution is increased in consequence of the ammonia which is removed by the evacuation (and which is, of course, recovered), and special care must therefore be exercised in the preparation of such solutions. In the case of other spinning solutions, the time-saving action of the vacuum cannot be used in consequence of the high vapour pressure of the solvents, and the air must be removed by long storage (ripening) of the spinning solution.

It is only in the case of the manufacture of the entirely new material known as “air silk” that evacuation is unnecessary; this material is an artificial silk which, at a casual glance under

the microscope, resembles natural cellulose fibres (see Fig. 3 (i), page 26), and which is produced by Glanzstoffabriken, Elberfeld; in the manufacture of this material, air or inert gas is introduced by mechanical or chemical means, in a state of fine distribution, before spinning. Even so, very special measures are required in order to obtain the necessary degree of smallness of the bubbles when manufacturing "air silk," so that they may pass through the fine spinning apertures without causing rupture of the fibre. In the case of this product, the bubbles must, therefore, be largely removed in the first instance, or brought into a very highly divided condition.

In order to be able to spin the solutions, certain conditions must be fulfilled; when such a solution is drawn out into a thin thread, this thread must not disintegrate into individual drops, but must steadily and evenly decrease in diameter. The better such a solution allows itself to be drawn out, if, for example, the spinning solution is allowed to fall from a glass rod which has been dipped into the solution, the better are the mechanical properties, in general, of the artificial silk threads produced from such a solution. Such conditions are only fulfilled if, apart from other necessary properties, the spinning solution has a definite viscosity.* As is often the case

* Regarding the investigation of wood pulp, see C. G. Schwalbe and R. Sieber, *Die chemische Betriebskontrolle in der Zellstoff- und Papierindustrie*, Second Edition, 217-281 (Julius Springer, Berlin, 1922); H. Jentgen, *Laboratoriumsbuch für die Kunstseide- und, Ersatzfaserindustrie*, Halle, 1923. The method of E. Schmidt and E. Graumann (*Ber.*, 21, II, 1860 (1921)), for the determination of the lignin contents of wood by means of chlorine dioxide, may also be used for the determination of the degree of purity, together with the determination of the pentosans and hexosans soluble in alkali (see also section on "Wood Pulp.") We may also refer here to L. G. Bright's "Colour Reaction with Benzopurpurin," *Pulp and Paper Magazine of Canada*, 14, 645 (1926); Bright's solution consists of (1) 2.7 gm. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 100 c.c. distilled water, (2) 3.29 gm. potassium ferricyanide in 100 c.c. distilled water, and (3) 0.6 gm. "Du Pont Purpurin 4B, special" (quite free from alkali, soda or potash) in 100 c.c. of water. The sample of paper prepared for the investigation is treated for 20 minutes in a beaker at 20° C., with 10 c.c. of (1) + 10 c.c. of (2), and then well washed in a gentle stream of distilled water. The paper is then dyed with the dyestuff solution (3) at 45° C., and the fibre examined under the microscope, after drying if intended to be kept for reference. Any lignin which is present exercises a reducing action with production of Prussian blue, whilst fibre free from lignin is dyed to a brilliant red colour. On account of its interest we also mention here the fluorescence of unbleached sulphite pulp in ultra-violet light which was discovered by O. Gerngross, *Papierfabrikant*, 25, 49 (1927); this is apparently

in colloidal solutions, the viscosity of spinning solutions is reduced by purely mechanical treatment, apart from the other influences mentioned on page 12.

The viscosity is not usually determined in the capillary apparatus of Ostwald, used for scientific investigations, on account of the magnitude of the viscosities in question. The viscosimeter of Cochi^{us} is much used, and can be employed in the following simple form. Two marks, at a distance of 25 or 50 cm., are made on a glass tube of exactly 20 mm. bore. The tube is closed at both ends with patent fasteners, such as are usual on beer and soda water bottles; it is filled with spinning solution in such a manner that a sufficiently large air bubble remains in the tube.* The time is then measured which is required for this air bubble to rise from one mark to the other, the temperature being, of course, recorded. The bore of the tube is of considerable importance, and must, therefore, be absolutely correct. If necessary, tubes which are not of the correct bore must be calibrated by comparison with a viscosimeter of exactly the right dimensions, and the marks must be adjusted according to this calibration.

Other methods are also practised; for example, the measurement of the time of fall of a sphere of defined diameter and weight, such as a steel ball between two marks, in a tube of a definite width which is filled with the spinning solution; and also the measurement of the time of discharge of a definite volume of the spinning solution from an aperture of definite width which discharges from a pipette-shaped glass tube of definite length and width. All these methods can be used successfully. The viscosimeter of Cochi^{us}, in the simple form indicated above, has been found eminently suitable in practice. As, however, changes in the viscosity sometimes occur,† in the case of measurements which follow one another rapidly,‡

caused by the absorption of small amounts of tannins from the sulphite liquor by the cellulose fibres. This fluorescence is destroyed even by weak bleaching, and can, therefore, unfortunately not be used as a test for purity in that case.

* O. Faust, *Zts. f. physik. Chem.*, 103, 74 (1919).

† Zsigmondy, *Kolloidchemie*, 5th Edition, Part I, p. 210 (Spamer, Leipzig, 1925).

‡ See also H. Freundlich, *Kapillarchemie*, 3rd Edition, pp. 741 *et seq.* (Akademische Verlagsgesellschaft, Leipzig, 1923).

particularly in the case of very highly ripened viscose solutions, we mention especially the rotary viscosimeter* of Couette,† which is used, for example, in the laboratory of the Eastman Kodak Co. in a modified form, due to Sheppard,‡ which is described by The Svedberg.§

Gaebel|| carried out viscosity measurements of viscose in the Kaiser Wilhelm Institut for Fibre Investigation, by means of the rotary viscosimeter of Couette, in the laboratory of R. O. Herzog, and found that in the case of viscose, an elastic opposing force¶ is produced with increasing age which causes an apparent increase of the viscosity. (See also H. R. Kruyt** on "Lyophilic Colloids and Poiseuille's Law.") For the manufacture of artificial silk the uniformity of the viscosity, and other factors, from day to day, is naturally of great importance. We will return to this question later.

* R. Liesegang, *Kolloidchemische Technologie*, p. 147 (Steinkopff, Dresden and Leipzig, 1927), Section by H. Vogel, "Viskosimetrie kolloider Lösungen."

† *Ann. de chim. et de phys.* (5), 21, 433 (1890).

‡ S. E. Sheppard, *Gelatin in Photography*, p. 196 (1923).

§ *Kolloidchemie*, in German translation by Finkelstein, p. 205 (Akademische Verlagsgesellschaft, Leipzig, 1925).

|| R. Gaebel, Dissertation, Berlin, 1924; *Kolloid-Zts.*, 35, 193 (1924).

¶ O. Faust and G. Tammann, *Zts. f. physik. Chem.*, 71, 51 (1910).

** H. R. Kruyt, Zsigmondy celebration number (*Kolloid-Zts.*, 36, 218 (1925); regarding viscosimeters, see also W. Ostwald, *Kolloid-Zts.*, 48, 190, 210 (1927).

According to Kruyt, the capillary viscosimeter is theoretically as definite and as suitable as the apparatus of Couette, whilst it undoubtedly offers experimental advantages over the latter. According to Ostwald, the special anomalies found when using the Couette apparatus, which are not found when using the capillary viscosimeter, are due to special features of the former apparatus. The author also prefers the capillary viscosimeter, or under practical conditions with very viscous solutions, the viscosimeter of Coehius, which depends on the same theoretical principles, on account of the simplicity and certainty of its operation.

See also J. Scheiber, *Lacke und ihre Rohstoffe* (J. A. Barth, Leipzig, 1926), pp. 481, 519.

CHAPTER III

THE SPINNING PROCESS

Precipitation and Outline of Cross-section (Degree of Rotundity).

The spinning liquid must not only be capable of being drawn out to a fine thread, but must be of such a character that the liquid can rapidly be coagulated during the spinning process. This property is, of course, not common to all solutions which show a sufficiently high viscosity and which can be sufficiently drawn out, and for this reason solutions of cellulose or cellulose esters have so far alone been found suitable. Apart from the capability of being rapidly coagulated, the question of the strength of the coagulated fibre is, of course, of great importance for the spinning process. It is necessary that the strength should immediately be at least so great that it is possible to convey the coagulated fibre farther and to wind it round a suitable receiving contrivance.

As already mentioned, the extruded solution must be coagulated by some means in order to fix the extruded fibre. This coagulation occurs either by evaporation of the solvent (in the case of cellulose nitrate, acetyl cellulose and cellulose ethers) or by the removal of a component of the solvent, more particularly when using solvent mixtures, by passage through a precipitation bath in which the solvent or a component of the same is readily dissolved.

Thus, for example, cellulose nitrate, dissolved in a mixture of alcohol and ether, can be precipitated by spinning into an aqueous bath by the immediate removal of a large portion of the alcohol. The same kind of precipitation, but of a somewhat milder character, may also occur in the so-called "air spinning" process, already referred to; thus, for example, the much more volatile ether evaporates so rapidly in the air that the solvent power of the residual components of the solvent no longer suffices, and the dissolved material is precipitated. These precipitations are, of course, reversible, and the fibre

which is produced can always be brought into solution by addition of the solvents which have been removed. In the case of viscose solutions, also, such a reversible, or almost reversible, precipitation can be carried out by salting out, for example, with solutions of ammonium salts. The fibre so produced is of a jelly-like consistency, at any rate immediately after precipitation, and can be redissolved without difficulty.

An essentially different manner of precipitation is that in which the solutions of cellulose compounds are chemically altered by the action of chemical reagents, for instance in a precipitation bath, as, for example, when spinning cuprammonium cellulose solutions into sodium hydroxide solution or similar baths, or when spinning viscose solutions in baths of mineral acids. In these cases, a more or less elastic, fine tubular structure is produced round the stream of spinning solution injected into the precipitation bath, which may consist, for example, of cellulose hydrate, that is, of gelatinous cellulose, when viscose is spun into liquids containing mineral acid.* The interior of the tube-like structure is filled by unchanged spinning solution which is now separated from the precipitating bath by a semi-permeable membrane; in this case two separate processes occur, which are determined by the rate of diffusion of the precipitating agent through the semi-permeable membrane, on the one hand, and by the mutual osmotic effect between the spinning solution and precipitating bath, on the other. The character of the formation of the fibre differs entirely when the one or the other process predominates. The velocity of diffusion of the precipitating bath, which decomposes the spinning solution, can be greatly influenced by the addition of certain substances to the bath, as in the author's invention, described in French patent 612,879 of the

* According to recent investigations of R. O. Herzog (*Ber.*, 60, 600 (1927) and *Zts. f. physik. Chem.*, 127, 108 (1927)), cellulose is precipitated in the form of cellulose hydrate in all cases in which cellulose as such or in the form of compounds (cellulose nitrate or acetate) is precipitated from the dissolved state. This discovery is in good agreement with practical experience, and should yield food for thought to those who hope to obtain an artificial silk which would have the properties of cotton with regard to resistance to water and gelatinizing properties by applying the present methods of spinning to an exceptionally concentrated cellulose solution.

Köln-Rottweil A.G.* and the corresponding British patent 277,716, assigned by the author to the I. G. Farbenindustrie A.G.

The surface tension developed between the spinning solution and the precipitating bath is also alleged to play a part in the formation of the fibre. The addition of naphthalene sulphonic acids, alkylated in the naphthalene nucleus, to the precipitation bath or to the spinning solution or to both of these, is alleged to have a useful effect by reducing this interfacial surface tension.†

Osmotic action can naturally also occur when spinning reversibly precipitated cellulose ester solutions, such as those of cellulose nitrate or acetate, in any liquid which exercises a strong osmotic effect, apart from the removal of solvents already referred to; in this case also, the extruded solutions become surrounded by a tube-like structure of more or less pronounced semi-permeability. For physico-chemical reasons, it is obvious that in the wet-spinning process, apart from the temperature and concentration of the spinning solution and the character of the precipitation, the temperature and concentration of the precipitating bath have a decided influence on the form of the cross-section. This is less influenced by the distance traversed in the precipitating bath, although this also has some influence, because the concentration and temperature of the adherent precipitating bath which is carried along by the fibre, are constantly altering on account of the continued reaction. On the other hand, colloid-chemical considerations show that the colloid-chemical condition of the spinning solution, for example, the degree of ripeness of viscose solutions, that is, the particle size, together with the viscosity and the rate of shrinkage, are important factors in determining the form of cross-section.

But other quite specific actions of certain metallic salts in the precipitation bath have been discovered, for example, when spinning viscose. In this connection, the investigations of E. Hatschek‡ on the forms which drops and eddies of

* Identical with Austrian patents 108,122, Class 29B of the I. G.-Farbenindustrie A.G.

† R. Sapitz, E. Pott and F. Pospiech, British patent 280,608/1927.

‡ E. Hatschek, *Naturw.*, 15, 385 (1927); *Proc. Roy. Soc.*, Series A, 95, 303 (1919); see also O. Faust, *Die Seide*, 32, 263 (1927).

gelatinizing liquids assume in various coagulating solutions are of great practical interest, although carried out for entirely different purposes.

The specialist can frequently discover the manner in which fibre formation has occurred, and which of the above factors have had most influence on the process, from microscopic sections of the fibre, which for this reason are frequently used to determine the origin of specimens of artificial silk. The determination of the origin is no longer quite simple nowadays, as the viscose silk industry of the whole world now employs the process of the Vereinigte Glanzstoffabriken Elberfeld.* Even so, there are often certain differences in the cross-section which are due to variations in the above-mentioned factors in various works. Fig. 3 shows a series of microscopic cross-sections† which vary considerably. For comparison, a cross-section of real silk is shown in Fig. 3a. All these cross-sections are represented at a magnification of 400.

Real silk has a very small cross-section, which is only attained by very few artificial silks. Its cross-section is fairly rotund (see "Degree of Rotundity" at the end of this section). This is also the case for the finer qualities of artificial silk. The degree of rotundity is usually lower in the case of artificial silks of greater fibre thickness; that is, in the latter case a circle described about the cross-section of the fibre has a considerably greater area than the cross-section itself.

Fig. 3b shows the cross-section of a cellulose nitrate silk of the Belgian Tubize Works. The degree of rotundity is in this case smaller, in agreement with the greater thickness of the fibre. Rounded contours are typical of cellulose nitrate spun by the air-spinning process. This closely resembles the cross-section in Fig. 3c of the French acetate silk, "Rhodiaséta," which is also spun by the air-spinning process, that is, without the use of a precipitating bath.

* Vereinigte Glanzstoffabriken A.G., German patent 287,955/1912, is still valid until 1934.

† Regarding the practical production of cross-sections and the embedding of the fibre for the production of these in special cases, see A. Herzog, *Melliands Textilber*, 8, 254, 602 (1927), and *Die Kunstseide*, 9, 558 (1927), where a very practical and rapid method for the production of cross-sections of fibres is described; see also the book of the same author referred to in the Appendix, and H. Fikentscher, *Melliands Textilber*, 8, 933 (1927).

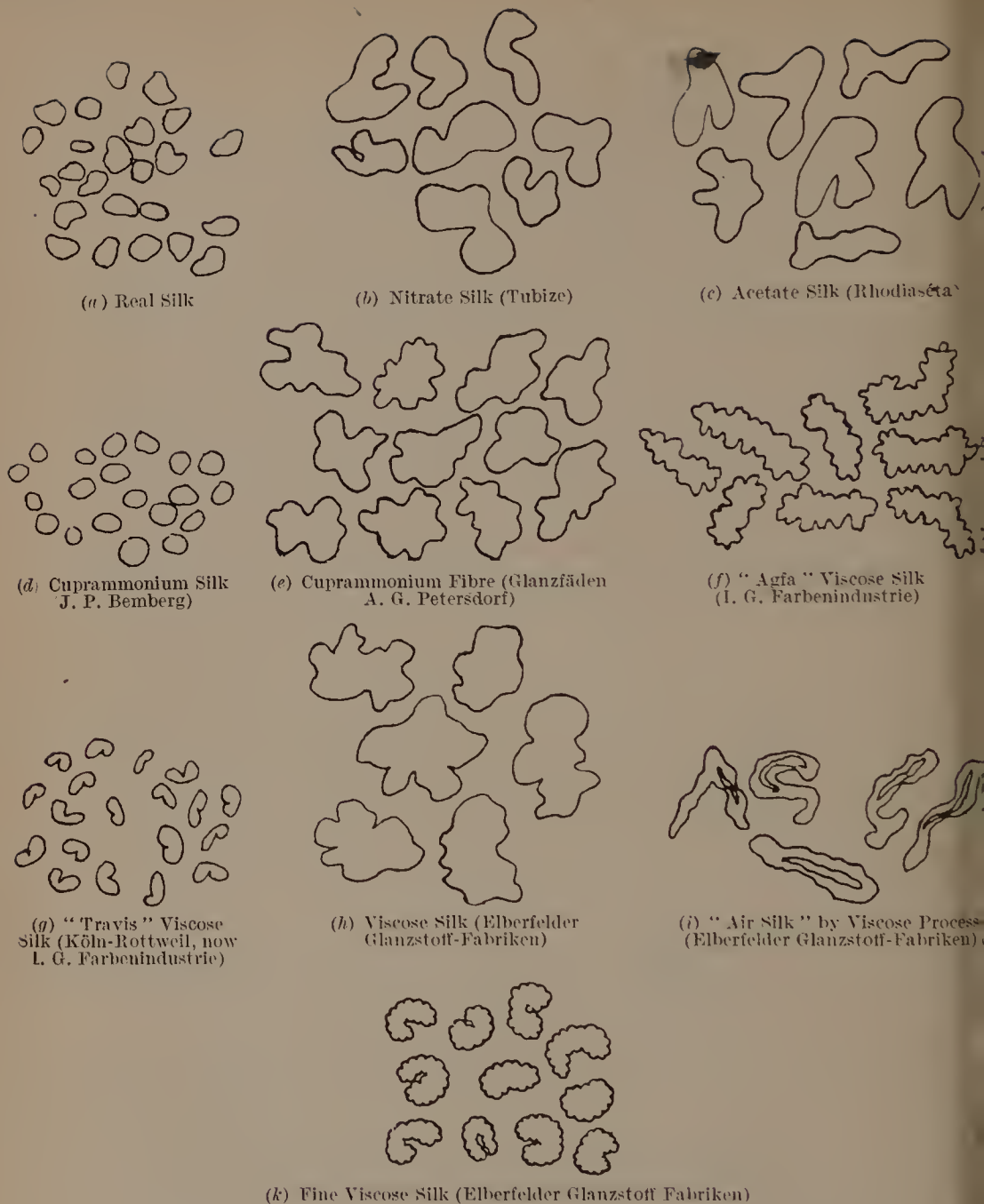


FIG. 3*

* Regarding influence of precipitating bath on form of cross-section, see also A. Herzog, *Leipziger Monatshefte f. Textil industrie*, 9, (1926); also *Textile Forschung*, 8, 87 (1926). On the influence of salt in the precipitating bath for viscose silk on the form of cross-section, see also P. Karrer and P. Schubert (*Helv. Chim. Act.*, X, 430 (1927)), who investigated a series of silks prepared by I. I. Stoeckly. See also cross-sections of British, Belgian, Swiss, and German acetate silk, by A. Herzog, *Die Kunstseide*, 9, 10 (1927), and K. Goetze, *Die Seide*, 32, 97 (1927).

Fig. 3*d* shows the cross-section of a very fine cuprammonium silk produced by the firm of J. P. Bemberg. In this case also, the degree of rotundity is considerable, but the individual fibre is no coarser than that of real silk. Fig. 3*e* shows the cross-section of a cuprammonium silk of the Glanzfäden A.G., Petersdorf i. Rsgb., which has a considerably greater fibre thickness and also a relatively small degree of rotundity. Figs. 3*f* to 3*i* represent cross-sections of viscose silks; Fig. 3*f* shows a viscose silk of the A.G. für Anilinfabrikation (I. G. Farbenindustrie A.G.).

Fig. 3*g* shows the cross-section of Travis silk, which is of a degree of fineness otherwise unknown in the viscose silk industry. The process of its production was developed during many years in the Vereinigte Köln-Rottweiler Pulverfabriken, which has since 1920 been known as the Köln-Rottweil A.G., and has turned its entire attention since the War to the production of artificial silk and other artificial fibres; the work was carried out in the Premnitz Works, and was taken over by the I. G. Farbenindustrie A.G. at the end of 1926, when the Köln-Rottweil Co. was absorbed by the latter. The cross-section of this silk is kidney-shaped.

Fig. 3*h* shows the cross section of a viscose silk of the Vereinigte Glanzstoffabriken Elberfeld, which is also characteristic.

Fig. 3*i*, finally, shows the cross-section of a so-called "air silk," also produced by the Vereinigte Glanzstoffabriken Elberfeld, and which has recently been placed on the market by that Company and by the closely allied Kunstseidenfabrik Emmenbrücke, Switzerland; this is a new product of peculiar handle and appearance.

In this case, an attempt has been made to reduce the degree of rotundity and to imitate the cross-section of cotton, and has been to a considerable extent successful. The material has a character of its own, but so far has proved weaker than other products, although a definite advance has recently been made in this direction.

Fig. 3*k* shows a cross-section of the fine viscose silk of the Vereinigte Glanzstoffabriken Elberfeld. This silk is probably

the finest silk produced by the old viscose process from ripened viscose, the titre of the individual fibre being 2.0 (see page 42). The cross-section, which is well developed, is remarkable on account of the fine indentations.

As might be supposed, the strongly indented cross-section causes a characteristic effect when the fibre is observed directly under the microscope. The microscopic view of such a fibre shows numerous furrows, whilst a fibre the cross-section of which shows no indentations has a glassy appearance similar to that of real silk.

The degree of rotundity is of importance, in so far as artificial silk produced from cellulose has a specific gravity which is about 10 per cent higher than that of real silk. The specific gravity of the latter when degummed is about 1.33 to 1.37, whilst that of acetate silk is 1.3 to 1.5, and the specific gravity of dry artificial silk from cellulose is 1.56 to 1.57. According to A. Herzog,* the specific gravity of Küttner silk is 1.51, and of Tubize silk 1.56. According to H. Brunswig,† the specific gravity of cotton is 1.58.‡ It is thus clear that artificial silk fibres of exactly the same dimensions as natural silk fibres have a correspondingly higher weight, and as the sale of silk at works

* *Mikroskopische Untersuchungen der Seide und Kunstseide* (J. Springer, Berlin, 1924).

† *Das Rauchlose Pulver*, p. 16 (Walter de Gruyter & Co., Berlin, 1926).

‡ Quite recently, "Pyknometric Measurements in Benzene," by P. Karrer and P. Schubert, *Helv., Chim. Act.*, 1928, gave the following results for the specific gravities of various fibres—

Artificial silk (cellulose)		1.5
Cotton		1.5
Natural silk		1.36
Wool		1.3
Acetate silk		1.3

G. Joseph Davidson has recently determined the specific volumes of mercerized cotton purified with soda solution and of artificial silk (*Journ. Textile Inst.*, 18, T. 175, (1927)). He found that the structure of cotton was loosened by mercerization and still more so when converted into artificial silk. His figures, re-calculated in terms of specific gravity, are given below—

Upland cotton purified with soda		1.567
" " mercerized		1.550
Sea island cotton purified with soda		1.558
" " " mercerized		1.546
Viscose silk		1.548
Cuprammonium silk		1.531
Nitrate silk		1.543

is based on the weight* and not on the length, the question of the degree of rotundity is of some practical importance.

It would, however, be wrong to attach too much importance to the production of a particularly low degree of rotundity when producing artificial silk. This fact is exemplified by the practical importance of Bemberg silk, which is due to the high qualities of this product, in spite of its high degree of rotundity.

It is never possible to draw conclusions from the cross-section of an artificial silk fibre regarding its quality, either in respect to chemical strength and elasticity or to its lustre. Two fibres of identical or similar cross-section may show extraordinary differences in physical properties.

The spinning nozzles are provided with a varying number of fine apertures ; the individual fibres expelled from the apertures of one nozzle are collected on a suitable contrivance. After completion of the spinning process, these fibres are twisted, and then form the actual artificial thread, consisting of a varying number of individual fibres of varying thickness.

Stretching During the Spinning Process. It is obvious that during the spinning process the speed at which the expelled fibre is introduced into the precipitating bath, and the speed at which it is removed from the same, are of great importance. In general, in all spinning processes the rate of withdrawal is greater than the rate of extrusion of the spinning liquid from the spinning aperture. Stretching therefore occurs, and can be determined directly by measurement according to the equation $b - a = s$,† where b is the rate of withdrawal, a the rate of expulsion of the liquid from the nozzles, and s the amount of stretch. If in these figures b is taken as 100 metres, then s is the percentage of stretch.‡ In some spinning processes

* See section on "Determination of Strength," pp. 44-53.

† In this equation the varying degree of shrinkage which occurs in consequence of the coagulation, and which is sometimes only completed after the thread has been wound on to the receiving contrivance, is ignored.

‡ This stretching process is well known in the textile industry in connection with the production of threads from short staple fibre, for example, from cotton, and the degree of stretching is then called the draft. In this case, the draft is the difference of the peripheral speed of two working pulleys of the drawing frame.

the degree of stretch is very considerable, and such processes are, therefore, called "stretch" spinning processes; but it must be remembered that to a certain extent all spinning processes are, in fact, stretch spinning processes.

Obviously, solutions of acetyl cellulose and cellulose nitrate, which can be reversibly coagulated from their solutions in organic solvents by slow evaporation of portions of the solvent during spinning, are particularly suitable for the stretch spinning process, and in this respect they have achieved a certain importance. It has been found possible to obtain very fine artificial silk from cellulose nitrate, and the very finest quality is now obtained from solutions of cellulose acetate.

Among the other spinning solutions, cuprammonium cellulose solutions in particular are capable of being drawn to very fine threads in the coagulating bath, as they coagulate relatively slowly. The stretch spinning process was, therefore, first practised with such solutions (Thiele's stretch spinning process, German patents 154,707/1901 and 179,772/1906), and is operated in Germany by a considerable number of works, including J. P. Bemberg, Fr. Küttner, and Hölkenseide G.m.b.H.

The viscose process was for years found less suitable as a stretch spinning process, as the precipitation with mineral acid baths, which is the only one practicable, is so energetic that it was impossible to stretch the fibres until they were very fine. The art of producing very fine fibres from viscose solutions has only recently been learned, by using viscose solutions of relatively high viscosity and containing relatively little cellulose. Glanzfäden, A.G., worked on these principles according to their German patent 389,394, according to which viscose solutions of considerably higher viscosity than usual were obtained by the omission or reduction of the ripening period of the alkali cellulose; the solutions contained about 5 per cent of cellulose only, as compared to the usual $7\frac{1}{2}$ to 8 per cent, and were spun in a bath of mineral acid; but this process alone did not lead to success. This was only attained by combining it with the use of special precipitation baths, according to the patents of the Vereinigte Glanstoffabriken,* who used sulphuric

* German patent 430,358/1919.

acid together with aromatic sulphonic acids or aromatic sulphonic acids condensed with formaldehyde ; or, those of the Köln-Rottweil A.G. (French patent 612,879, see page 27), or of Kämpf,* or of Faust and Kämpf.† The process of the author, assigned to I. G. Farbenindustrie, and described in German patent 452,697 of that firm, may also be mentioned here. It is also described in O. Faust's Swiss patent 106,908/1925, and British patent 229,518, and describes the production of fibres from the spinning solutions with the help of nozzles of non-metallic material.

The finer the thread which is spun and the finer the apertures from which the spinning solution is extruded, the more careful must be the filtration of the latter in order that blockage of the nozzle openings may be avoided as far as possible. It should also be noted that the spinning solutions, which are more or less highly viscous, tend to retain gas and air bubbles, and that if these are not removed they may cause rupture or a weak spot in the fibre extruded from the aperture when the bubbles come into contact with the latter. For this reason it is necessary to de-aerate the spinning solutions carefully if an artificial silk of good quality is to be obtained. (See page 18.)

On studying the spinning process closely, the observer is inevitably reminded of the analogy which it shows to the production of wire from metals by the use of draw-plates. In wire-drawing, the crystallites of the metal are broken down and arrange themselves in a position in which their longest axes are parallel to the axis of the wire.‡ The main difference between the two processes is that the spinning solution does not consist of the thread-forming substance only, but of a solvent in addition, and that chemical decomposition

* British patent 184,449/1922.

† O. Faust and A. Kämpf, German patent 431,846/1922. Compare also the numerous patents of Bronnert, which are the property of the Vereinigte Glanzstoffabriken, according to which the rate of decomposition is regulated by adjusting the concentration of the precipitation bath, and which are said to enable fine threads to be produced from such viscose spinning solutions as had previously been used, an aim which has also been achieved very successfully by the Vereinigte Glanzstoffabriken.

‡ G. Tammann, *Lehrbuch d. Metallographie*, 3rd Edition (Leopold Voss, Leipzig), p. 100.

or reaction sometimes occurs through the action of the precipitation bath.

The Spinning Solution and the Precipitated Fibre in Polarized Light. X-ray Diagrams. It might be assumed that in so far as the colloidal micellae have a rod-like or plate-like form, they must orientate themselves in a definite manner during spinning under influence of the liquid flow and of the tension. According to the investigations so far carried out by the author,* it appears, however, that this is not the case, at any rate in the case of the strongly hydrated and gelatinized particles which are present in colloidal suspension in viscose solutions. The author was unable to observe double refraction in the flowing liquid† or the Majorana phenomenon‡ (double refraction in the magnetic field).

The author was also unable to observe the character of the particles under the ultra-microscope, for example, in viscose solutions, as the difference in the refractive indices of the dispersed and continuous phases was too small.

The existence of particles can be detected by means of an artifice as follows: Viscose is mixed with a colloidal gold solution; the particles of gold are absorbed by the viscose and largely lose their brownian movement, although otherwise the tint and appearance of the liquid remain unchanged. As, however, the number of particles absorbed by each viscose particle cannot readily be determined, this method requires special precautions if it is to be used for the determination of the number of particles. In any case, the absence of molecular movement shows that the particles in the solution must be fairly large. §

* O. Faust, *Ber.*, 59, 2919 (1926); *Zellulosechemie*, 8, 41 (1927).

† H. Zocher, *Zts. f. physik. Chem.*, 98, 293 (1921); Freundlich, Diesselhorst and Leonhardt, *Elster-Geitel Festschrift*, 435 (Brunswick, 1925).

‡ Majorana, *Rend. Acad. d. Lincei*, 11, 1, 536, 539 (1902).

§ The cellulose formula, recently discussed by K. Freudenberg, page 14, which makes use of Haworth's ring formula for glucose, enables one to imagine a cellulose micella of considerable size; it may also be assumed that in the dissolved condition the individual components, which consist of glucose residues united to one another in chains by means of oxygen atoms, may be orientated so variably that no anisotropic effect occurs. This may also be the case during coagulation. As shown by the experiments already described, a directive effect is not produced by frictional forces in the flowing solution, even if the friction is very considerable, for coagulation under tension is

The unpublished X-ray investigations carried out by the author at the Scherrer Institute in Zurich in 1921 dealt with technical cellulose nitrate, denitrated cellulose nitrate silk, acetate silk and staple fibre from cuprammonium solution and from viscose silk, and did not indicate a regular crystalline structure of the thread.* Commercial artificial silk threads, however, show orientated double refraction.† The fibres are illuminated between crossed nicols in the polarization microscope,‡ whilst the cross-sections appear dark.

Cellulose hydrate films obtained from viscose show a similar double refraction to artificial silk threads, whereas cellulose nitrate films show no double refraction, contrasting in this way with cellulose nitrate threads. However, cellulose hydrate films and threads which show no double refraction may be obtained from viscose, by avoiding any tension during their preparation. Any double refraction which may be present vanishes entirely or partially on nitrating the double-refracting threads or films, and the behaviour of these products differs in this way from that of natural fibres, such as cotton. If, however, the threads are maintained under tension during nitration, and in this case only, double refraction remains to a greater or less extent; such fibres then show a so-called "fibre diagram" on X-ray investigation.§

necessary for this purpose, in which case Freudenberg's theory conforms to the assumption of a more or less marked orientation with a possible fixation of various strains and deformations of the micellae.

* See also R. O. Herzog and W. Janke, *Ber.*, 53, 2162 (1920).

† H. Ambronn, *Kolloid-Zts.*, 18, 90, 273 (1916); 20, 173 (1917); 44, 1 (1928); and Ambronn and Frey, *Das Polarisationsmikroskop, seine Anwendung in der Kolloid-forschung* (Leipzig, 1926), 111-118.

‡ A. Herzog, *Die mikroskopische Untersuchung der Seide und Kunstseide* (Springer, Berlin, 1924), 61 *et seq.*

§ See also R. O. Herzog and H. W. Gonell, *Kolloid-Zts.*, 35, 201 (1924); 125 (1911). The above-mentioned facts do not conflict with the observations made by R. O. Herzog and his fellow workers. The highly nitrated technical cellulose nitrate containing 13.1 per cent N, and investigated by me, showed no crystalline interference phenomena in spite of an exceedingly well retained fibrous structure. By very careful nitration and preservation of the original fibrous structure, R. O. Herzog and S. v. Náray-Zzabo (*Zts. f. physik. Chem., Cohenband*, 616 (1927)), apparently obtained the fibre diagram corresponding to cellulose trinitrate only, with percentages of nitrogen varying from 4.41 to 13.31; this showed a definite relationship to the fibre diagram of cellulose itself, so leading to conclusions regarding the position of the hydroxyl groups in the elementary cellulose aggregates. After denitration, the diagram of the original native cellulose was re-obtained. If, however, mercerized ramie

An analogous phenomenon was observed by I. R. Katz,* who obtained X-ray diagrams of india-rubber and gelatin (see also I. R. Katz and O. Gerngross)† in the normal and in the highly-stretched condition. The diagrams indicate an amorphous structure in the normal unstretched condition, whilst the diagram of a crystalline fibre can be observed when these substances are highly stretched. Herzog and Gonell‡ point out that according to investigations of Freundlich and Oppenheimer§ and those of Zocher, slight strains, such as those caused,

fibre was used as the raw material, points corresponding to mercerized cellulose occurred in the diagram. After strong mercerization the diagram was very indefinite, and the fibrous structure may undergo strong disturbances after nitration; this fact explains the result obtained by me with technical cellulose nitrate. In the case of acetyl cellulose, Herzog and Janke (loc. cit.) at first obtained no interference (having previously dissolved these materials), thus agreeing with my observations (R. O. Herzog, *Helv. chim. Act.*, 9, 631 (1926)): whilst later point diagrams were obtained in a parallel position with the diagram of ordinary cellulose after saponification, thus resembling cellulose nitrate, whilst dissolved or dispersed cellulose nitrate or acetate, after spinning to form a fibre and subsequent saponification, show the X-ray diagram of mercerized cellulose hydrate (R. O. Herzog, *Ber.*, 60, 600 (1927); *Zts. f. physik. Chem.*, 127, 108 (1927)). These fibres were prepared by the dry spinning process and had also undergone the stretching which is now usual in practice. In general, the fibres spun from cellulose compounds with stretching, after saponification and regeneration of the cellulose, yielded X-ray diagrams characteristic of cellulose. Regarding the methods of X-ray investigation, the application of which in all fields has become of such great importance for the furthering of scientific knowledge, see more particularly: H. Mark, *Die Verwendung der Röntgenstrahlen in Chemie und Technik* (J. A. Barth, Leipzig (1926)); R. Glocker, *Materialprüfung mit Röntgenstrahlen* (Springer, Berlin (1927)). For the sake of completeness, we may also refer here to the extremely interesting investigations of R. O. Herzog and G. Laski (*Zts. f. physik. Chem.*, 121, 136 (1926)) on the absorption spectra of cellulose and mercerized cellulose, and of the cellulose nitrates obtained from these, in the ultra-red, which showed typical absorption bands, which are identical for cellulose and mercerized cellulose and are also found in the cellulose nitrates, although their relative intensities are somewhat changed in this case. As in this case, also, no alteration is caused by mercerization, Herzog concludes in view of the dispersion experiments above referred to, and those in salt solutions, by P. P. v. Weimarn (*Report of the Imperial Industrial Research Institution, Osaka, Japan*, 18, 174 (1925)), that mercerization primarily represents a physical attack only, on the structure of the cellulose crystal. In this connection it would be of interest to investigate the diagram of ripened alkali cellulose.

* *Kolloid-Zts.*, 36, 300 (1925); 37, 19 (1925).

† O. Gerngross and I. R. Katz, *Naturw.*, 13, 901 (1925); *Kolloid-Zts.*, 39, 181 (1926).

‡ R. O. Herzog and H. W. Gonell, *Zsigmondyfestschrift*, *Kolloid-Zts.*, 36, 44 (1925).

§ H. Freundlich and Oppenheimer, *Ber.*, 58, 147 (1925).

for example, by polishing glass surfaces, cause dichroism, from which they conclude that very small forces are required in order to produce an ordered crystallization.

I. R. Katz considers it uncertain whether in his experiments a pseudo-crystalline amorphous or a crystalline condition is produced. H. Ambronn* was able to identify in some varieties of natural cellulose—but not in all—the appearance of slip-planes, which is characteristic of crystalline substances and which can so well be demonstrated in metals† when the lower elastic limit is exceeded ;‡ but he could in no case discover these in artificial silk fibres.

Ambronn points out that there are quite definite intermediate stages between crystals conforming to the strict definitions of classical crystallography, and those structures which may be described as definitely crystalline but in which the regular external boundaries are lacking ; he describes these latter as “semi-crystals”§ in accordance with the nomenclature of F. Rinne.

* H. Ambronn, *Zsigmondyfestschrift, Kolloid-Zts.*, 36, 119, 127, 128 (1925).

† O. Faust and G. Tammann, *Zts. f. physik. Chem.*, 75, 108 (1910).

‡ O. Faust, *Zts. f. Anorg. Chem.*, 78, 201 (1912), Figs. 13 and 17.

§ The usual English expression is “crystallites” (*Translator*).

CHAPTER IV

FIBROUS STRUCTURE, LUSTRE AND COLOUR

It will be evident from the foregoing that the finished artificial silk fibre consists of a colloidal gel which possesses a micro-structure varying with the manner of its production. This micro-structure is dependent, on the one hand, on the colloidal structure of the spinning solution, and on the other hand, on the manner in which this is converted into a fibre and coagulated. One must assume a more or less cellular structure, such as has been determined by the well-known investigations of Zsigmondy and Bachmann on gelatin,* colloidal silicic acid† and other substances.

The investigations of O. Hahn and M. Biltz on the gels of the hydroxides of iron, aluminium, thorium and zirconium are of interest in this connection.‡

During coagulation chemical processes naturally occur together with colloidal processes, and vary according to the character of the spinning solution. Processes which cause the evolution of gaseous products or of products insoluble in water as a result of chemical decomposition are of special importance ; such a process takes place, for example, with viscose, which yields carbon disulphide on decomposition, whilst simultaneously the trithiocarbonate, which is always present as an impurity in viscose solutions, yields carbon disulphide and hydrogen sulphide. When such solutions are decomposed too violently and too rapidly, these gaseous products are unable to escape in a very finely divided form from the structure during coagulation ; they therefore collect with formation of blister-like cavities which may cause rupture of the surface of the fibre.

This process can be plainly seen in the appended Fig. 4,

* *Kolloid-Zts.*, 11, 145 (1912).

† W. Bachmann, Inaugural Dissertation, Göttingen (1911), *Zts. f. anorg. Chem.*, 13.

‡ M. Biltz, Lecture at the 89th Naturforscherversammlung at Düsseldorf, 1926, on experiments of O. Hahn and M. Biltz ; see also the lecture of M. Biltz at Hanover, *Zts. f. angew. Chem.*, 40, 786 (1927).



(5509)

FIG. 4. VISCOSE FIBRE, DECOMPOSED BY MINERAL ACID (Mag. 1400)

which shows a viscose fibre, obtained by violent decomposition in mineral acids, at a magnification of 1,400. One can plainly distinguish the funnel-shaped openings which have been produced in the surface of the fibre by the separated particles of gas and liquid. These chemical processes obviously also occur when the fibre is less violently decomposed, but in this case the separation of the by-products occurs in such a finely divided condition that they are no longer visible, even under the microscope, and are able to escape through the channels due to the cellular structure of the fibre.

Its more or less marked lustre is an important quality of artificial silk. Apart from the index of refraction,* the power of reflecting light is mainly dependent on the character of the surface of artificial silk or of its individual fibres. The index of refraction must be the same for all artificial silks consisting of cellulose. According to A. Herzog, its value is 1.595 for real silk, 1.527 for cuprammonium silk, 1.524 for viscose silk, 1.515 for cellulose nitrate silk and 1.479 for cellulose acetate silk. Real silk therefore occupies a special position in consequence of its high refractive index and the increased amount of totally reflected light rays due to this quality. The lustre varies according to the thickness of the individual fibres and also according to the character of the surface, whether smooth or channelled (see the representations of cross-sections, page 26), or whether the surface is more or less freely perforated by the gas bubbles which escape during manufacture, as described in the preceding section. A very smooth artificial silk thread will readily transmit incident light and appear transparent and glassy if the individual fibres are not very fine. Analogous relations consist, for example, between white snow and a large ice crystal. According to the preceding explanation, fibres with highly irregular cross-section should have a white, opaque appearance and a good optical covering power. The covering power may, of course, also be modified by the artificial production of precipitates in the fibre,† or by

* See also A. Herzog, *Die mikroskopische Untersuchung der Seide und der Kunstseide*, pp. 71–81 (J. Springer, Berlin (1924)).

† H. Karplus, Czecho-Slovakian patent application, 4302/1926.

the separation of sulphur,* for example, in viscose fibres. The lustre may also be modified by the same conditions; it is now usual to weaken and soften the lustre in accordance with the prevailing fashion.†

For the determination of lustre, the gloss-meter of Zart is‡ usually employed (Fig. 5). It is supplied by Janke & Kunkel, Cologne. This extremely simple apparatus enables the "white

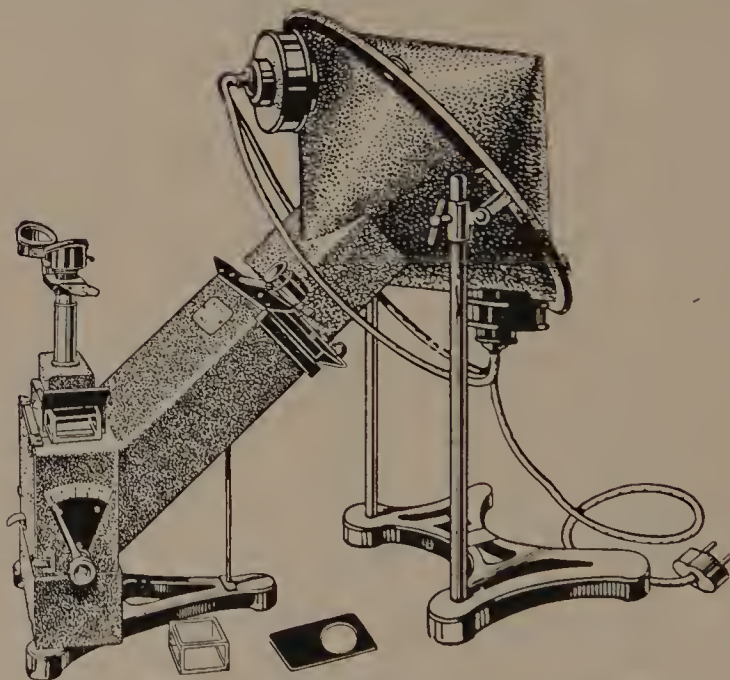


FIG. 5. WILHELM OSTWALD'S HALF-SHADE PHOTOMETER

Adapted by Zart as Gloss-meter
(Suppliers: Janke & Kunkel A. G., Cologne)

contents" of the diffuse reflected light from a fibre to be determined, and also the sum of the diffuse and directly reflected light; the difference between the diffuse and the directly reflected light measures the gloss of the fibre under investigation.

We may also refer to the apparatus described by H. Schulz§

* Comptoir des Textiles Artificiels, Czecho-Slovakian application 300/1927.

† Courtaulds, Ltd., British patent 273,354/1926; Borvisk Syndicate, Ltd. (London), British patent 273,647/1926.

‡ A. Zart, *Melliands Textilberichte*, 4, 161, 218 (1923).

§ *Melliands Textilberichte*, 6, 25 (1924); *Papierfabrikant*, 36, 509 (1927).

which is supplied by Goerz, Berlin, or in a newer form by the Askania-Werke A.G., Berlin.

When determining the lustre of a textile sample or of silk fibre wound in several layers, for example, on a cardboard support, it is soon observed that the value found depends on the position and direction of the sample under examination. Those directions which show the greatest differences in the results are at right-angles one to another. In order to eliminate this very comprehensible phenomenon it is advisable to rotate the sample sufficiently rapidly. A Klughardt* has recently studied the important question of the measurement of lustre in detail on the basis of theoretical considerations and has placed it on a broader scientific basis. He used for his measurements the well-known step photometer of C. Pulfrich,† which enables very accurate measurements to be made, and which has been largely used in technical practice for the determination of the shade of colour and of the contents of black and of white in the light from coloured surfaces. As the varying intensity of daylight on various days and at various times may cause considerable differences in measurement, amounting to 20 per cent, a constant artificial source of light should be used and may usefully be provided with a daylight filter. The quantity of light received by the sample under investigation from the light source is the greater the more nearly the angle a (see Fig. 6 on page 40), which the plane of the sample makes with the horizontal plane, approximates to 45° . The ratio of this "inclined brightness" to the fundamental brightness is equal for all ideal matte bodies for a given value of a ; when determining the degree of lustre this ratio must be deducted from the ratio of inclined brightness to fundamental brightness, as determined for the body under examination. The number so obtained is Klughardt's "gloss number," which attains a maximum for an angle of inclination of 20° to 25° and becomes zero when a is approximately 45° , and negative for larger values of a . Klughardt indicates the characteristic variation

* *Zts. f. techn. Physik.*, 9, 109 (1927); see also *Leipziger Monatsh. f. Textilind.* 43, 1, 121 (1927); *Die Seide*, 23, 233 (1927).

† C. Pulfrich, *Zts. f. Instrumentenkunde*, 45, 35 (1925).

of the gloss number, for all surfaces which have not too high a lustre, by the position and magnitude of its maximum and the determination of the angle at which it becomes zero. The determination of one lustre measurement only, for one definite angle of inclination, is not sufficient to form an opinion on the lustre.

According to Klughardt, the measured brightness of barytes white at the customary inclination of 22.5° is 1.352, if the brightness measured in a horizontal position is designated as 1.

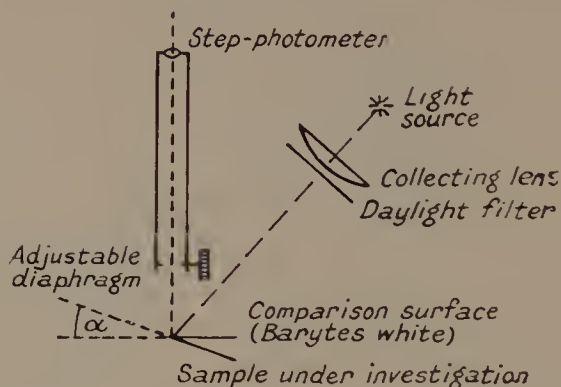


FIG. 6

Even barytes white is not ideally matte, but possesses a small amount of lustre.

The lustre of fabrics is, as already mentioned, very dependent on the direction, more particularly in the case of very fibrous materials and long-fibred textiles such as plush. In order to determine the lustre in such cases by placing the sample under the photometer, H. Naumann,* instead of obtaining an average value by rotating the sample as described above, obtains several values, for example, four, at angles differing by 30° ; for each measurement the sample is turned by 15° until it has turned through a total of 180° , and Naumann so obtains a lustre-curve expressed in co-ordinates in the ordinary manner; to ensure reliability these measurements are carried out on several samples of the same material. In this case also, as already mentioned, the measurement by Klughardt's method

* *Zts. f. wiss. Photographie*, 23, 303 (1925).

must be carried out at several inclinations α ; H. Naumann measures at inclinations of 0° to 50° at intervals of 10° .

— When measuring coloured samples, the colour must be determined by the use of corresponding colour filters by the method of W. Ostwald.* On the measurement of the colour of lustrous surfaces, see more especially A. Klughardt,† who uses the conception of “relative brightness” in place of Ostwald’s “black contents.”

* *Farbenlehre* (1919).

† *Leipziger Mschr. f. Textilind.*, 42, 312, 357 (1927).

CHAPTER V

PROPERTIES OF THE FIBRE

Titre. Silk is characterized for the purpose of the textile consumer by its so-called "titre." The unit of titre is the denier, and there are two different deniers, the Italian denier and the French, or so-called "legal" denier. According to the Italian system a thread or fibre has a thickness of 1 denier if a thread 9000 metres long weighs 1 gramme. According to

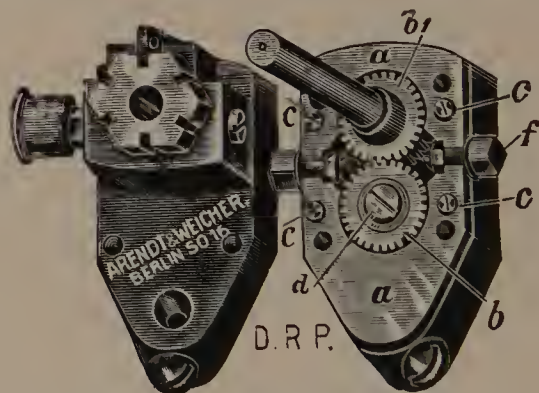


FIG. 7. GEAR-WHEEL PUMP (OPENED)
(Arendt & Weicher)

the French or "legal" titre system, 10,000 metres of a 1-denier thread weigh 1 gramme.

For the sake of comparison we may mention that real silk has a titre of about unity,* so that 9000 metres of real silk weigh 1 gramme. If a silk thread is composed of 25 individual fibres it therefore has a total titre of 25. The titre of artificial silk fibres varies from 1 to about 10 deniers. Ordinarily it is from 5 to 8 deniers.

In order to ensure uniformity of titre when spinning artificial silk, so-called "titre pumps" are used, which ensure a uniform supply of spinning solution to each spinning nozzle. Small gear-wheel pumps are ordinarily used for the purpose, and are

* This is according to the Italian scale, which is now in general use, as it conforms with the actual condition of natural silk.

supplied, for example, by Arendt & Weicher, Berlin, S.O.16 (see Fig. 7), or by the Deutsche Orthopädische Werke, Berlin, S.W. 68. The firm of F. A. Neidig, Mannheim, also supplies satisfactory gear-wheel pumps. The right-hand side of Fig. 7 shows the action of such pumps. The upper gear-wheel b_1 is turned by means of the attached outwardly projecting axle in a clockwise direction; its teeth engage very exactly and are very accurately ground to fit the chambers in which

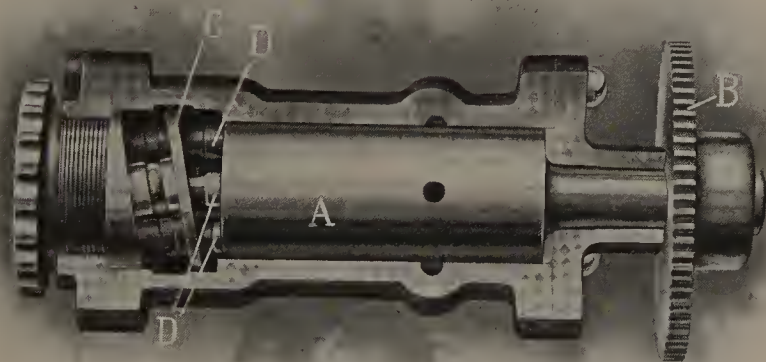


FIG. 8. PISTON SPINNING PUMP
Werdohler Pumpenfabrick (A. Hillebrandt)

they turn, so that a vacuum is produced in the right-hand chamber of the pump and, consequently, the spinning solution is drawn in through the opening shown closed with a screw f on the right-hand side of Fig. 7, which is connected with a supply pipe. The spinning solution so drawn in fills the spaces between the teeth of the cog-wheels and is transported by these, when the wheels revolve, into the left-hand chamber of the pump, into which it is driven when the teeth engage, and is forced out at the left-hand side of the chamber through the opening with which this is provided and which is connected with the pipe leading to the spinning nozzle. In order to avoid strong compression of the liquid when the gears engage,

F. Eggersdörfer* provides a draining channel at this point for the purpose of preventing heavy wear of the teeth. O. Winkler† constructs the gears of double the usual width and provides the drive with a small addition, which ensures that the pumps, which are mounted on the same driving shaft shall have the same output. As is evident from these pro-

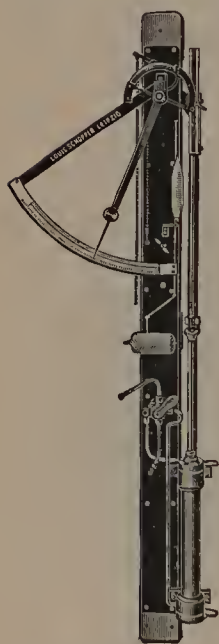


FIG. 9
SERIMETER
(Schopper)

posals, the pumps are liable to show an undesirable degree of wear and tear, which influences their output and therefore the quality of the thread which is produced, more particularly with regard to uniformity. In good gear-wheel pumps the gears engage very closely, so that pressures of 10 to 12 atmospheres may easily be attained in the spinning solution. In an artificial silk works, continuous control of the pump output is absolutely essential in order to ensure production of uniform quality.

Piston spinning pumps are also used and are supplied, for example, by the Werdohler Pumpenfabrik Paul Hillebrandt, Werdohl. i. W. (Fig. 8), and are particularly suitable when using spinning solutions of relatively low viscosity. In multi-cylinder pumps, such as the one shown, the revolution of an obliquely placed headpiece *C* causes the piston *D* to enter or recede from the cylinder, by which means the spinning solution is expelled or aspirated. The cylinders (with pistons) are contained in the revolving cam *A*, which is turned by the gear-wheel *B*.

The strength of artificial silk is almost always determined by the apparatus supplied by the firm of Louis Schopper, Leipzig (Fig. 9). This apparatus enables not only the breaking load of an artificial silk fibre to be determined, but also its elongation at the breaking load, which is of practical importance. Qualities of artificial silk with too small an elongation

* German registered design 1,006,674 (1927).

† German registered design 1,010,271 (1927).

(under 10 per cent) are liable to cause difficulties when treated by textile machinery.

The true elasticity, that is, the reversible elongation under load, generally, at any rate, appears to be extremely small for artificial silk in contrast to real silk, and is seldom determined

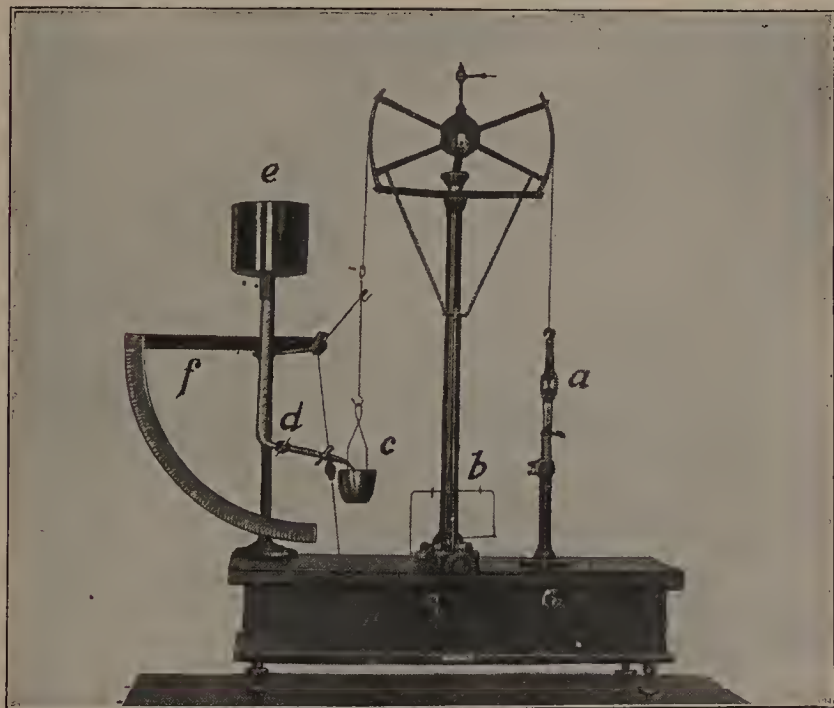


FIG. 10

in practice. In industrial artificial silk laboratories it has only been investigated for scientific purposes; and it has been found that on gelatinization of apparently over-stretched silks this elongation is removed, and is, therefore, really reversible. Recently, W. Weltzien* has communicated data of an interesting character on this subject.

Apart from the determination of breaking load and elongation, the degree of twist which is imparted to the artificial silk thread during manufacture is also usually determined in practice. For this purpose also, the firm of Schopper supplies very suitable apparatus. A new contrivance with an

* *Die Seide*, 32, 365 (1927).

automatic release of the elongation indicator on serimeters (instruments for determining the breaking load) is described by H. Vollprecht,* of the Textil-Forschungs-Institut, Dresden. P. Kraiss† has described an apparatus for the determination of the breaking load, elongation and torsional resistance of individual fibres, which is protected by German patent application 727,686/42K, and is supplied by Hugo Keyl, Dresden A. Marienstrasse. In this apparatus (Fig. 10) the load is supplied by a stream of water. We may also specially refer here to the new Tänzer-Polikleit recording fibre dynamometer,‡ which is supplied by Paul Polikleit, Halle (Fig. 11). The dynamometer is constructed in the form of a balanced lever, the supporting point of which lies at the top of the graduated column *a*. The lever arm *b*, with vernier *b*₁, indicates the load on the scale *c*. The right-hand half *h* of the beam carries at *d* the clip *e* for the fibre *f*. The other, left-hand, half of the beam terminates in a pen *m*, which records the variations of the load on the drum *k*, without appreciable friction. The load is supplied either by a clockwork *n* actuating the shaft *o*, or manually by the handle *r* attached to the top of the same shaft. The clockwork *n* can be reversed for the purpose of raising or lowering. By this means it is possible to study the phenomena which occur during loading and subsequent relaxation, and to record everything that takes place. The elongation is measured on the scale *p*. The suspension *e* is very practically arranged so that the point of support may remain unaltered with increase of load; this is ensured by attaching the suspension to the end of a band *g*, which passes over a circular arc *h*₁. This arrangement had already been adopted in the dynamometer of Kraiss, shown in Fig. 10, and also in the serimeter of Schopper, shown in Fig. 9, which latter is not, however, suitable for testing individual fibres.

When determining the breaking load in the wet condition in this apparatus, it is advisable to attach a loop in the path of the clamped thread of about 1–2 mm. internal width, and

* *Leipzig, Mschr. f. Textilind.*, 42, 63–64 (1927).

† *Textile Forschung*, 3, 86 (1921); see also F. Rühlemann, *Papierfabrikant*, 25, 577 (1927).

‡ *Melliands Textilberichte*, 8, 858, 938 (1927).

10 mm. or more in length, which is split at the end. This loop can be brought into action by folding it downwards, when a drop of water is applied to it and is held by capillary action. The thread is first tested in the dry condition, and succeeding

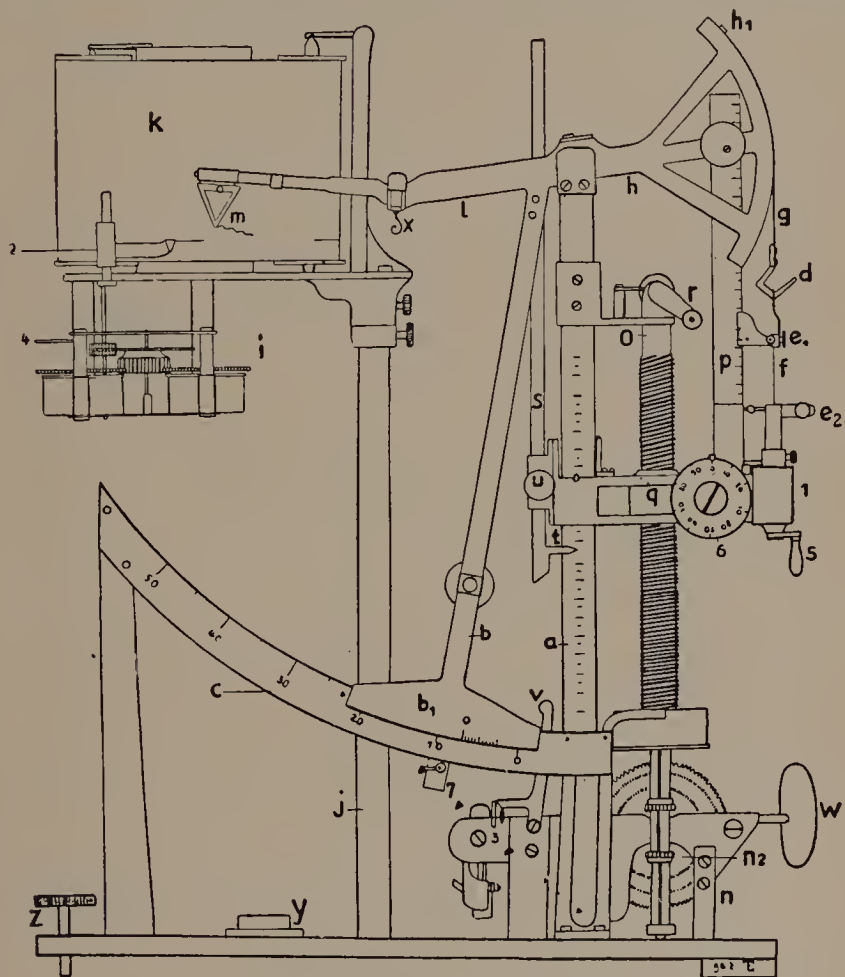


FIG. 11. FIBRE DYNAMOMETER
(Tänzer-Polikleit)

sections of the same thread are then tested wet by bringing the loop containing the drop of water into the path of the clamped thread, so that the thread absorbs water throughout the length of the loop. For this purpose about 45–60 seconds are required. By all other methods of determination of the breaking load when wet, values which are too high are easily

obtained, more particularly in the case of individual fibres, as the moisture easily dries again before the determination is completed. Values which are too low may also be obtained by damage to a previously moistened thread, whilst it is being fixed in position. If the elongation in the moist condition is also to be determined, this can be achieved by laying a thoroughly wetted strip of filter paper along the whole length of the thread between the clips, by which means partial drying can be avoided.

A certain degree of elongation is important for artificial silk threads, and, in fact, more important than an abnormal degree of tensile strength, as during working, and particularly in knitting operations, the elongation is called into play, and if this is too small breakage of the thread occurs. An elongation of 12 to 16 per cent may be considered sufficient. Too great an elongation is also undesirable, as it gives rise—particularly during weaving—to a very ugly and prominent defect known as shiny wefts,* which may often only be noticeable in the finished fabric, when individual weft threads which have too high an elongation are subjected to tensile stress. This effect can easily be produced artificially for purposes of demonstration.

The elongation, that is, the percentage increase in length at the breaking point, must not be confused with the true elasticity, that is, with that elongation under tensile stress which disappears automatically, that is, without any treatment with a liquid, when the load is relaxed. This elasticity, which imparts such valuable properties, for example, to real silk, is very small in amount in the case of all artificial silks, and hardly exceeds 1 to 2 per cent of the length in the best qualities. It can be determined without any difficulty.

It should be noted that the rate of increase of the load is of importance in determining the tensile qualities. There are no recognized standards in regard to this matter. When testing artificial silk threads in Schopper's apparatus, the load is produced by a piston which falls slowly, and to the upper end of which a clamp is attached for holding the thread. Usually the piston is caused to drop through a distance of 20 cm. in a

* See also H. Vollprecht, *Leipzig. Mschr. f. Textilind.*, 43, 60, 133 (1927).

period of 15 seconds. These rates of increase can easily be adjusted in the forms of apparatus described. If the tests are carried out sufficiently slowly the rate of loading may vary within certain limits without affecting the uniformity of the determinations. Naturally, the length of thread used and the rate at which the load is applied must be mutually comparable in each case. In order to determine the commercial value of artificial silk the normal constants with regard to breaking strain and elongation are insufficient. According to the *Textile World* (New York), No. 11, Vol. 71 (March, 1927, p. 47, "elasticity" denotes (percentage elongation) $\times$ (moisture content) $\times$ (tensile strength in the dry condition in grammes per denier); thus, for example, $20 \times 0.65 \times 2 = 26$, or $25 \times 0.55 \times 1.3 = 17.88$. The former silk is the better. Lustre and degree of whiteness cannot be incorporated in the formula.

Attempts have recently been made in Germany to standardize methods of investigation of artificial silk. This is a desirable development, as in many cases the methods adopted are of a very elementary character. In all cases, however, the opinion of the purchaser will naturally be ultimately decisive. (See also *Die Kunstseide*, 9, 623 (1927).)

As is the case with natural fibres, artificial silks contain amounts of moisture which vary with the degree of saturation of the air. In the case of viscose and cuprammonium silks; natural silk, wool and cotton, these data have been determined by Obermiller (1925)* with the following results—

Relative saturation of air with water vapour in percentages at 20° C.	2.5	35	55	75	92	97	100
Percentage of moisture in artificial silk	2.5	8.5	12.5	17.5	28	38	>40†

The figures which he obtained for cotton and for real silk are

* J. Obermiller, *Melliands Textilberichte*, 7, 75 (1925).

† According to the author's experience these figures vary somewhat for artificial silk fibres from various sources, which also vary in the degree of swelling when moistened.

considerably lower, whilst for wool they are higher (up to 80 per cent of saturation.)

In consequence of the considerable dependence of the breaking load and elongation of artificial silk on the degree of saturation it has been agreed that these figures shall be quoted for an atmospheric saturation of 65 per cent and that the data shall as far as possible be determined under this condition. The accurate adjustment of the degree of saturation offers considerable difficulties, and the work of Obermiller* in overcoming these has been particularly valuable. The degree of saturation of the atmosphere can be accurately measured with Assmann's aspirating psychrometer or with capillary hygrometers which have been calibrated by the former.† One may, however, obtain satisfactory results in practice by obtaining, once and for all, a curve connecting tensile strength and degree of moisture, that is, an elongation-moisture curve for the types of silk to be manufactured or to be used, and using this for correcting the measured values to 65 per cent saturation.

P. Kraus and E. Adams‡ investigated the elongation and tensile strength of viscose silk when perfectly dry and when containing various degrees of moisture, by first immersing the fibre in absolute alcohol and then in aqueous-alcoholic mixtures of various concentrations. They found that the breaking load in pure alcohol increased by 12 per cent, whilst the elongation decreased by 38.5 per cent; in pure water the breaking load was 60 per cent lower and the elongation 50 per cent higher than the figures determined in air at 65 per cent saturation. The elongation at rupture of artificial silk consisting of cellulose depends greatly on the tension employed during manufacture, but is usually about 50 per cent greater in the wet condition than when measured in air of 65 per cent saturation. This fact, which has for long been known to experts, has frequently led to the practice of exposing the fibre to an especially high tension during its precipitation, by which means the elongation

* J. Obermiller, *Zts. f. angew. Chem.*, 27, 904 (1924), German patent 396,296; *Zts. f. angew. Chem.*, 39, 46 (1926); *Melliands Textilberichte*, 5, 765, 818 (1925); 7, 75, 166 (1926); see also L. Kirberger, *Kunstseide*, 9, 142 (1927).

† W. Weltzien, *Die Seide*, 23, 175 (1927).

‡ See also P. Kraus, *Zts. f. angew. Chem.*, 39, 196 (1926).

is decreased but the breaking load increased. Such a method was already described by C. A. Ernst* in 1905 (see also Medenwald†). If this tension is applied to the fibre after it has been very rapidly and extensively solidified by coagulation or decomposition, as is always the case for viscose silk, no considerable change in the length or thickness of the spun fibre occurs. The micellae which are caused to cohere by coagulation undergo a certain permanent deformation which leads to the above-mentioned increased strength and decrease of elongation, and which affects the optical double refraction.‡

According to German registered designs 995,328, 995,329, 995,330 and 995,331 of 4th June, 1927, and 1,003,970 of 22nd September, 1927, the I.G. Farbenindustrie A.G. removes the point at which the thread is subjected to such a tension to the thread-guide itself. A "uniform" tension, as it is called in the description, is not, however, achieved by the arrangement described; what is actually achieved is essentially an increased tension, with the effect already mentioned.

We give below the data of investigations on a series of various artificial silk products which were carried out by R. Reinecke.§ As will be seen from this table, the physical characteristics of the various manufactured products vary considerably. For the sake of comparison we may add that real silk shows a breaking load of 3 to 3.5 grammes per denier and is, therefore, stronger than all artificial products and also stronger than natural cotton and all other natural fibres. The breaking load of natural silk when moist is about 75 per cent of its breaking load when dry and is, therefore, also higher than that of all other fibres. The elongation of real silk, according to J. Karger and E. Schmid,|| is 24 per cent at 50 per cent atmospheric saturation, 27 per cent at 70 per cent atmospheric saturation, and 32.7 per cent when wet.

* U.S. patents 808,148/1905, and 808,149/1905.

† R. Medenwald and Dynamit A.G. vorm. Nobel & Co., German patent 390,139, Class 29A (1922).

‡ The resistance of such threads to enzymatic action is also considerably increased compared with that of threads produced with little or no tension; (see O. Faust, P. Karrer, and P. Schubert, *Helv. Chem. Act.* (1928).

§ *Melliands Textilberichte*, 7, 543 (1926).

|| *Zts. f. techn. Phys.*, 6 (1925).

The tensile strength of individual fibres is generally found to be 0.1 to 0.2 gram. higher per denier titre than the tensile strength of an artificial silk thread produced from a considerable number of twisted fibres. The tensile strength of natural wool per denier is less than that of artificial cellulose fibres. The author found the tensile strength of wool to be 1.5 gram. per denier and the tensile strength when wet to be 78.7 per cent of that when dry. For cotton he found 3.5 gram. per denier when dry

TABLE II
(*Melliands Textilberichte*, VII, p. 543 (1926))
PHYSICAL DATA OF VARIOUS ARTIFICIAL SILK PRODUCTS
(Dr. R. Reinecke)

Firm	I. Titre	II. Percentage Variations	III. Number of fibres per thread	IV. Tensile Strength	V. Percentage Variations	VI. Strength when Knotted	VII. Elasticity	VIII. Percentage Variations	IX. X. Tensile Strength when Wet	
									Absolute	Relative %
Acetate silk	134	3.0	26 31	0.88	4.74	0.79	22.8	10.09	0.43	48.9
Agfa	184.5	7.3	24	1.27	6.53	1.18	21.3	9.9	0.56	44.3
Bayreuth	176	6.8	17 27	1.24	8.11	1.19	14.5	7.9	0.43	34.68
Bemberg twisted	113	4.4	68 95	1.60	4.31	1.47	12.1	4.13	0.86	53.55
Bemberg untwisted	122	3.3	—	1.51*	4.61	1.54	9.8	14.22	0.75	50.0
Borvisk	189	3.95	24	1.25	5.14	1.15	14.8	12.34	0.52	40.9
Giesches Erben	186	5.38	22 24	1.26*	2.65	1.26	26.5	3.02	0.57	45.44
Glanzstoff	147.5	1.4	24	1.45*	2.15	1.28	15.4	5.82	0.58	39.87
Glanzstoff	126	2.1	45 452	1.54*	3.09	1.34	10.3	2.91	0.58	37.7
Herminghaus	198	5.69	20 4	1.14	4.56	1.08	13.95	9.53	0.38	33.31
Kelsterbach	187	4.2	23	1.38*	5.08	1.27	24.9	4.42	0.42	30.43
Köln-Rottweil	191	2.09	18	1.09*	1.78	1.04	18.6	9.14	0.39	35.8
Köln-R., "Travis"	125	1.6	94 120	1.77	3.62	1.50	12.4	8.07	0.75	42.37
Küttner Viskose	179	3.35	24	1.25*	4.04	1.11	17.6	8.52	0.48	38.4
Küttner Zellvag	179	3.35	184	1.15*	3.64	1.11	13.4	8.21	0.57	49.74
Oberbruch	175	2.0	24	1.39	7.50	1.26	15.3	11.33	0.62	42.2
St. Pölten	123	3.6	18	1.26*	1.48	1.13	13.8	7.25	0.43	34.13
Rorschach	303	0.99	42	1.24	2.05	1.12	16.5	5.45	0.46	37.1
Spinnfaser A.G.	182	2.19	24	1.47	4.31	1.39	17.6	7.38	0.66	44.9
Spinnfaser A.G.	122	1.2	36	1.63	2.8	1.57	13.8	3.01	0.75	46.0
Spinnstoff Glauchan	179	5.04	28	1.78	3.35	1.47	14.6	8.44	0.75	42.8
Sydowsaue	190	0.53	25	1.21*	1.70	1.16	20.8	4.81	0.46	38.7
Viscose, Arnstadt	294	4.08	48-50	1.54	4.24	1.19	11.7	10.26	0.65	42.2
Zehlendorf	121	6.22	15-18	1.24	6.78	1.10	19.0	12.96	0.45	36.52
American Viscose	153	1.30	21	1.56	2.53	1.43	24.9	5.22	0.66	42.6
Arnheim	119	2.3	18	1.31*	1.54	1.27	16.8	8.33	0.50	38.2
Chatillon	151	2.66	21	1.19	3.95	1.01	12.7	7.87	0.49	41.18
Emmenbrücke	124	2.1	13	1.29*	1.25	1.01	18.1	2.76	0.32	24.81
Emmenbr. Kap.	304	3.4	ca. 100	0.68	0.82	0.63	13.2	6.82	0.18	26.47
Snia Viscosa	177	2.3	21-25	1.52	7.43	1.30	17.4	27.6	0.58	38.4
Tubize	186	3.8	24	1.23	6.5	1.10	13.7	8.0	0.45	37.8
Viscose Co. of Am.	151	0.66	18	1.28	5.42	1.20	20.6	6.28	0.46	35.94

The figures marked with an asterisk (*) must be considered as obsolete, as the present products of the firms in question now show considerably higher tensile strengths, the increases being as high as 0.3 in some cases.

and 117 per cent of this value when wet, that is, approximately the tensile strength of real silk, whilst its elongation was about 7 per cent only, and even when wet about 8.2 per cent only.*

Adsorptive Power for Dyestuffs. It is clear that the fibre structure is of special importance with regard to the dyeing properties and adsorptive power of a fibre for dyestuffs. If for any reason the structure of a fibre is not uniform, the adsorptive surface per unit of length and the adsorptive power of the fibre for dyestuffs will vary.† This condition is then indicated by uneven dyeing properties, which are the source of much worry to the industries which use artificial silk. A grave light is thrown on these difficulties by British patent 254,531/1926 of the large artificial silk firm, Courtaulds, Ltd. In this patent, the proposal is made to dye the whole output of silk with a sensitive dyestuff, to sort the dyed material, and then to remove the dyestuff by bleaching. However, the uniform dyeing properties of the artificial silk supplied by the leading artificial silk works of the world show that these works have acquired processes by which it is possible continuously to manufacture a uniform artificial silk. These processes, which have hitherto been kept secret in order to avoid competition, are explained in a very interesting article by A. Lehner and A. Jäger.‡ According to these investigators, any tension induced in the fibre during its production affects the adsorptive power for dyestuffs of the finished viscose silk in such a manner that, other things being equal, a more strongly stretched thread shows a lower adsorptive power for substantive and indanthrene dyestuffs, whilst basic dyestuffs are more

* According to H. Fikentscher (*Melliands Textilberichte*, 8, 856 (1927)), the elongation of cottons of various origin and quality varies considerably, the average of the better qualities being scarcely more than 10 per cent. When dealing with the same kind of cotton, fibres of higher tensile strength also show higher elongation, as might be expected. In the case of ordinary American cotton, he found that the tensile strength was 3.571 to 8.777 gm., the average being 5.308 gm.; the elongation 6.611 to 11.075 per cent—average 7.535 per cent. Variations in both these characteristics for the same kind of cotton therefore vary by almost 100 per cent; such considerable differences do not occur with good artificial fibres.

† See also the important communication of H. G. Dahlenvord, *Melliands Textilberichte*, 6, 739 (1925).

‡ *Die Kunstseide*, 9, 219, 264 (1927).

strongly adsorbed. This circumstance may be utilized in order to level up streaky dyeings by subsequent topping with basic dyestuffs. Variations in tension when spinning the viscose silk fibre, caused by variations of the length undergoing coagulation at a given instant, currents in the spinning bath, and so forth, cause unevenness in the dyeing properties. In consequence of this discovery, which was independently made by O. Faüst, and at his instigation, the I.G. Farbenindustrie A.G. applied for German registered designs 970,459, Class 29A, November, 1926,* and 994,386, Class 29A, of 4th April, 1927,† according to which the tension in the thread-guide is either reduced to a minimum or is made uniform by the resiliency of the thread-guide itself. The knowledge gained during these investigations is of particular interest to the colloidal chemist.

It is but natural, according to what we have already written, that the adsorptive power for dyestuffs of artificial cellulose fibres should vary according to their origin and manufacture; moreover, it is always higher than that of cotton. Wool dyestuffs, which are not adsorbed by cotton, are also occasionally adsorbed by artificial silk, though to a lesser degree, so that when dyeing mixed fabrics consisting of wool and artificial silk, in which the latter is not to be dyed, it is necessary first to test the dyestuffs to be used. In this respect acetate silk behaves more satisfactorily.

Those artificial silks which consist of cellulose are otherwise dyed in the same manner and with the same dyestuffs as cotton,‡ whereas acetate silk, in particular, at first offered great difficulties when attempts were made to dye it. The dyestuff manufacturers of Europe and America have now succeeded in producing a large number of dyestuffs for acetate silk, and the process of dyeing that material has been completely explained by the work of Kurt Hans Meyer.§ This process is a simple process of solution, apart from the

* *Die Kunstseide*, 9, 274 (1927); patent applied for.

† *Die Kunstseide*, 9, 422 (1927); patent applied for.

‡ The dyeing of cellulose fibres with substantive dyestuffs is a typical absorption process; (see also R. Zsigmondy, *Verh. d. Ges. d. Naturfreunde und Ärzte*, 73rd Meeting, Hamburg, 1901, p. 171; also W. Biltz, *Ber.*, 37, 1095 (1904)).

§ *Melliands Textilberichte*, 6, 737 (1925).

behaviour of basic dyestuffs, which represents an adsorptive process. C. G. Candlish* has described the practice of artificial silk dyeing, regarding which we must refer the reader to books and publications dealing with dyeing,† and more particularly to the directions published by the dyestuff manufacturers. We would more particularly refer to the interesting dissertation on colloidal-chemical factors in the substantive dyeing of cellulose, produced under the direction of W. Ostwald by J. Maschek (Leipzig, 1922).

The Modification of Tensile Strength by Chemical Action.

The tensile strength of artificial silk fibres is naturally partially dependent on their colloid-chemical micro-structure. It is not, however, dependent on this factor alone, as both the quality of the raw material and the manner in which the chemical process is carried out are of considerable importance for the strength and elongation of the artificial fibre. In any case, the manner in which the chemical process of artificial silk production is carried out, even within the normal limits, is not without influence on the cellulose, quite apart from the fact that the production of so-called "oxy-cellulose," for example, by too strong a bleaching of the silk, or the formation of so-called "hydrocellulose" by faulty treatment of the silk with acids, are of special influence on the physical properties. The concentrations at which various acids exert an injurious action have been determined by Krais and Biltz.‡ According to these investigators the following concentrations of acids are just permissible with the hydro-extracted fibre, and allow this to be dried without injurious action : Lactic acid, 1 per cent ;

* *J. Soc. Dyers and Colourists*, 43, 37 (1927) ; *Die Seide*, 32, 265 (1927) ; see also *Die Seide*, 23, 10 (1928) and C. E. Mullin, *Acetate Silk and Its Dyes* (Constable & Co., Ltd., London, 1928).

† We may mention, for example, P. Ruggli, *Praktikum der Färberei und Farbstoffanalyse* (J. F. Bergmann, Munich, 1925) ; W. Zanker, *Die Färberei* (Dr. M. Jänecke, Leipzig, 1922) ; F. Erban, *Laboratoriumsbuch für Färbereien Druckereien, Farben-, Lack-, und Papierfabrikanten* (W. Knapp, Halle, 1902).

Regarding the dyeing of artificial silk, we may also refer to the interesting communications of W. Weltzien and K. Götze (*Die Seide*, 31, 257 (1926), and 32, 401 (1927)), which are of special interest because they definitely show with absolute clearness that the dyeing of artificial silk is not absolutely identical with that of cotton, and that the fastness of dyestuffs on artificial silk is often different to that on cotton.

‡ *Textile Forschung*, 7, 61 (1925).

acetic acid, 0.3 per cent ; tartaric acid, 0.3 per cent ; oxalic acid, 1.0 per cent ; sulphuric acid, 0.05 per cent.

According to E. Ristenpart and K. Petzold,* who carried out experiments on drying viscose silk, cuprammonium silk and acetate silk, at 110° and 140° C., cuprammonium silk is less sensitive to formic acid than to lactic acid, and the same remarks apply to acetate silk, which in general is considerably less sensitive to acids. On the other hand, the sensitiveness of acetate silk to large temporary increases of temperature, such as are inevitable during ironing processes, is very great. Temperatures of 200° to 250° C. have a catastrophic effect. Artificial silk which has been damaged by acid shows greatly decreased strength and elongation, and its adsorptive power for dyestuffs is greatly reduced. Its properties of swelling in water and caustic soda solution are also much changed.

* *Die Kunstseide*, 9, 260 (1927).

CHAPTER VI

SWELLING POWER AND DETERMINATION OF DEGREE OF SWELLING

SWELLING (gelatinization) occurs by adsorption of a liquid into the interior of the swelling substance, and is accompanied by increase of volume of the latter, together with decrease in its tensile strength and increase of its elastic limits.* The total volume, that is, the volume of the substance which swells, plus that of the adsorbed liquid, decreases with liberation of heat (heat of swelling). I. R. Katz† has closely studied the laws of swelling of colloids in water.

According to Katz, the laws governing swelling are identical for both amorphous and crystalline substances. They are also identical for substances which swell to a limited or to an unlimited extent and even for the dilution of concentrated solutions, for example, of sulphuric acid, with water, although, as pointed out by R. Zsigmondy,‡ the latter process is dissimilar in character on account of the independent freedom of motion of all the molecules present, whilst in the swelling process the molecules and ultra-microns have not complete freedom of motion in consequence of a certain interdependence which is always present. The swelling pressure P —that is, the pressure which must be exerted in order to expel the swelling liquid from the swollen substance—can easily be calculated, according to H. Freundlich,§ from the vapour pressure h of the swelling liquid in the swollen substance, as follows—

$$P = - \frac{dV}{di} \cdot RT \log h \text{ where } V \text{ is the specific volume of the}$$

* R. Zsigmondy, *Kolloidchemie*, 5th Edition, Part I, p. 105 (Spamer, Leipzig, 1925).

† *Kolloidchem. Beihefte*, 9 (1917) (Steinkopff). A valuable supplement to this work is Martin H. Fischer, *Kolloidchemie der Wasserbindung*, 2nd Edition (Steinkopff, Dresden, 1927).

‡ R. Zsigmondy, *Kolloidchemie*, 5th Edition, Part I, p. 105 (Spamer Leipzig, 1925).

§ *Kolloidchem. Beihefte*, 3, 442 (1912).

dry (unswollen) substance, and i the amount of swelling liquid in grammes adsorbed by 1 gm. of the dried substance. A close and simplified approximation of the formula is $P = -1200 \log h$.

Figs. 12 to 14 show graphically measurements made by I. R. Katz on cellulose (Schleicher & Schüll's filter paper No. 589) of the variations of h and of the heat of swelling W with variations of i , and also the calculated values for the swelling pressure P with variation of i .

According to I. R. Katz* and I. R. Katz and H. Mark,† one can determine whether the swelling liquid is adsorbed between the micellae or in an intra-molecular form in solid solution; for in the first case the X-ray diagram is unaltered by the swelling process, whereas in the latter case it is altered. On this basis the caustic soda solution used for mercerization appears to be adsorbed in an intra-molecular manner, whilst water is merely adsorbed between the micellae.

The swelling of cellulose and wood pulp in particular have frequently been dealt with (see section on "Wood Pulp"). In order to determine the degree of swelling, one may make use of the increase in weight, as is more especially usual in the case of short-fibred celluloses and wood pulp; or one may determine microscopically the alterations in thickness or length of the fibres.‡ P. A. Thiessen and C. Carius§ have described a method by which the measurement of changes of thickness of films can readily be carried out.

A simple and practical method of determining the swelling of artificial silk fibres was, however, first described by W. Weltzien,|| who thus enabled the very important

* Koninkl. Akad. van Wetensch, Amsterdam, *Wisk. en Natk. afd.*, 33, 281-293 (1924).

† I. R. Katz and H. Mark, Koninkl. Akad. van Wetensch, Amsterdam, *Wisk. en Natk. afd.*, 33, 294-301 (1924).

‡ E. Heuser and R. Bartunek, *Zellulosechemie*, 6, 19 (1925); E. Heuser, *Lehrb. d. Zellulosechemie*, 2nd Edition, p. 18 (Gebr. Bornträger, Berlin, 1923). A. Oppé and K. Götze, *Melliands Textilberichte*, 6, 850 (1925). A. Herzog, *Textile Forschung*, 3, 10 (1925).

§ P. A. Thiessen and C. Carius, *Zsigmondy-Festschrift (Kolloid-Zts.)*, 36, 245 (1925).

|| *Mittlg. d. Textilforschungsanst. Krefeld*, I, 1 (1925); *Melliands Textilberichte*, 7, 338 (1926).

determination of swelling power to be introduced into the artificial silk industry. Weltzien measures the alteration in length of

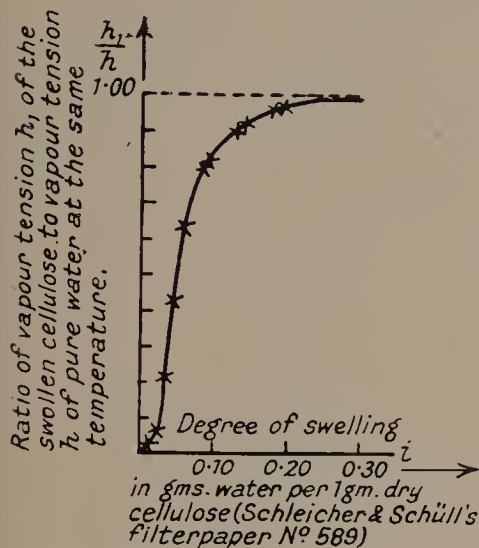


FIG. 12

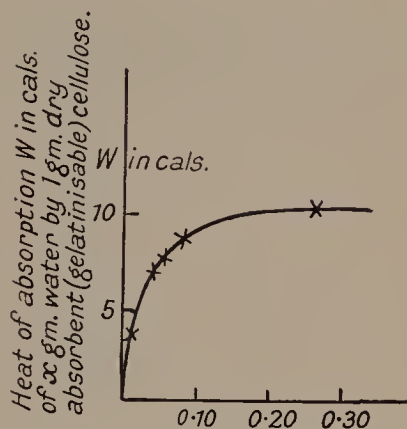


FIG. 13

a fibre about 50 cm. long, which is suspended in the swelling liquid. The method of experiment will be clear from Fig. 15.

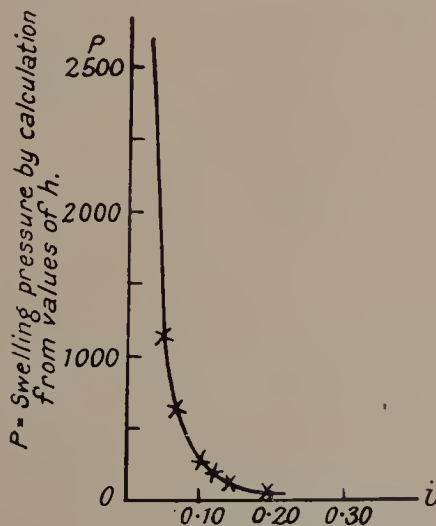


FIG. 14

A millimetre scale D , 50 to 60 mm. long, is inserted into a glass tube C , which is sealed below and is fixed by means

of the rubber stopper *B* into a glass tube *A* of 7 to 9 mm. bore. Into stopper *B* one or more glass rods *E* are inserted in such a manner that they can readily be adjusted in a vertical direction; they serve to support the silk fibres. *g* is a glass tube leading from a calcium chloride tower, through which dry air can be aspirated into *A* by means of the tube *H*

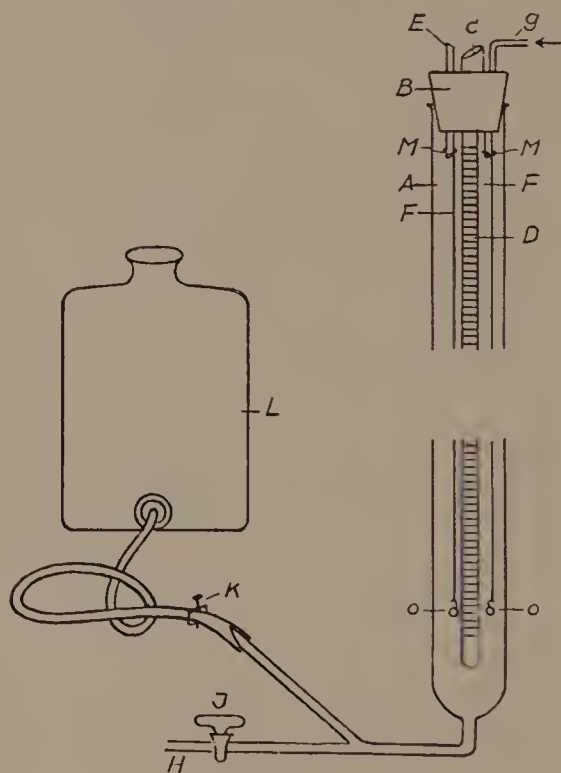


FIG. 15

sealed to its lower end. By closing the cock *J*, opening the pinch-cock *K*, and raising the bottle *L*, the swelling liquid can be introduced into the cylinder, in which it bathes the fibres *F*, the length of which has already been determined in dry air. The artificial silk fibres under test are fastened by small rubber bands at such a height that the point of attachment *M* coincides with the zero point of the scale *D*. The fibres are maintained under tension during the determination by glass beads *O*, of slight weight (0.40 gm.), which may contain mercury. Weltzien then noted the alterations in length of the artificial

silk fibres, which he investigated, during the following treatment—

$\text{Dry} \rightarrow \text{Water} \rightarrow \text{Caustic Soda Solution} \rightarrow \text{Water} \rightarrow \text{Dry}$
Swelling
Contraction

In Fig. 16 the average values of measurements carried out by Weltzien on viscose silk with three concentrations of sodium

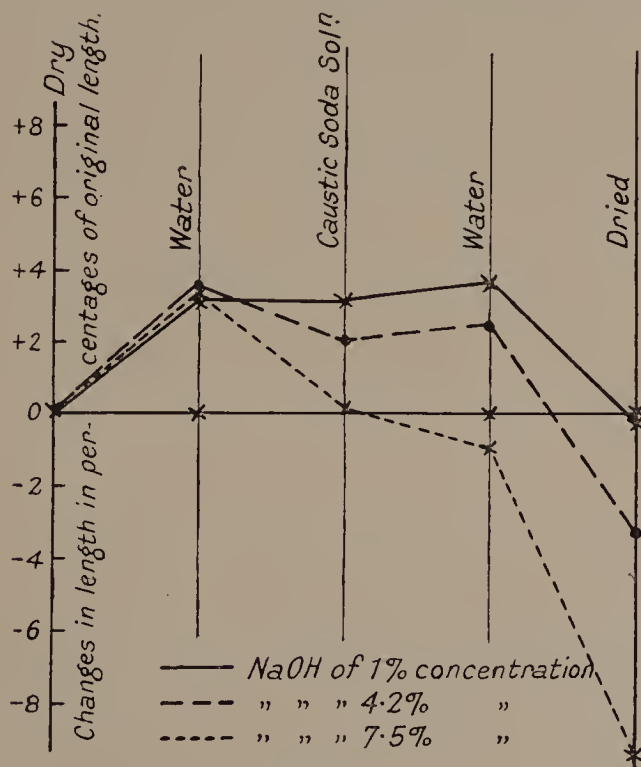


FIG. 16

hydroxide solution (1 per cent, 4.2 per cent, and 7.5 per cent) are reproduced in the very convenient diagrammatic form used by him. According to these results, the course of the curve is greatly dependent on the concentration of the sodium hydroxide solution used for swelling. The accuracy of the measurements is of the order of 0.1 to 0.2 per cent, and is thus very satisfactory. When using a definite concentration of sodium hydroxide the course of the curve is very uniform in the case of artificial silk of uniform manufacture, and any

large variations in the determinations with several samples of the same origin indicate with certainty a varying condition of the experimental material, which gives rise to varying degrees of adsorptive power for dyestuffs, as was pointed out by Weltzien. The second portion of the curves, that is, the portion showing the contractions, is reversible (see Figs. 17 to 21); this, according to Weltzien, indicates the equalization of internal strains previously produced in the fibre.

I have investigated these conditions, jointly with K. Littmann, making use of Weltzien's method.* The result obtained

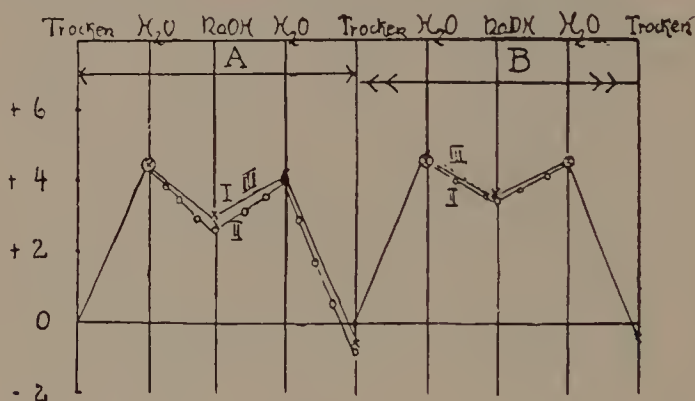


FIG. 17
("Trocken" = Dry)

was that artificial silk of uniform manufacture, and which therefore dyes evenly, also behaves quite uniformly when examined by this method. Fig. 17 shows the results of the examination of three different threads of similar manufacture, in which the first halves *A* of the curves show the behaviour during the first swelling and contraction, and the second halves *B* a repetition of this treatment; these show the reversibility of the swelling process, already mentioned by Weltzien.

Sodium hydroxide solution of 4 per cent concentration by weight was used as the swelling liquid, and was found to be very suitable for these investigations, as at higher concentrations the threads are easily broken. Fig. 18 shows the behaviour of threads I and III of Fig. 17, after they had first been loaded

* *Zellulosechemie*, 7, 166 (1926).

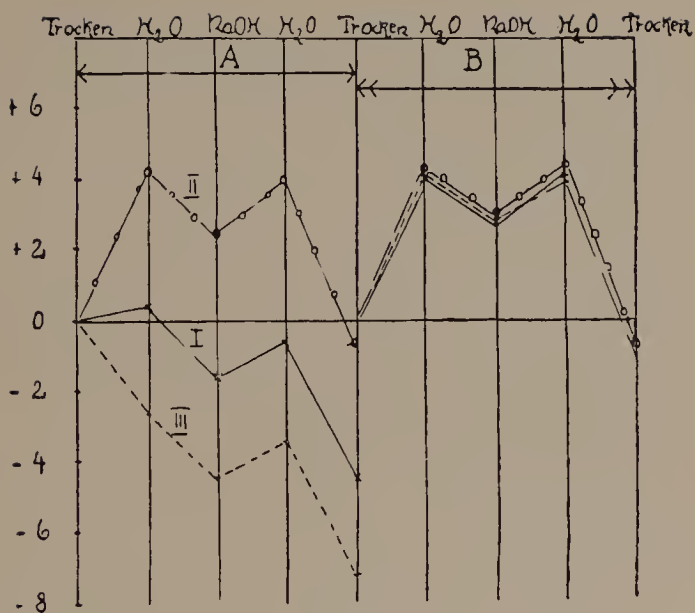


FIG. 18

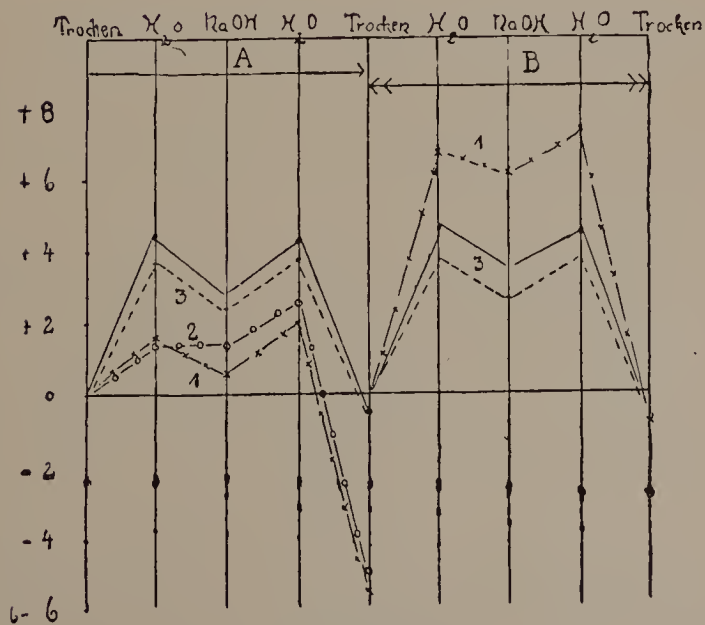


FIG. 19

("Trocken" = Dry)

in the air-dried condition with 50 and 100 gm. and thus stretched; the breaking load was about 100 to 200 gm. For comparison, the normal curve for thread II is inserted. The completely altered behaviour of the stretched threads no longer occurs after having once been swollen by the alkali, and when the swelling process is repeated in portion B of the curve they show absolutely normal behaviour. It may also be mentioned that these strongly over-strained threads show a slightly decreased absorptive capacity for substantive and indanthrene dyestuffs,* and it is evident that uneven dyeing due to such circumstances may occasionally be improved by careful treatment with alkaline liquors.

In the next set of curves (Fig. 19), the unnumbered curve represents the normal fibre. Fibre 1 was moistened with $\frac{1}{2}$ per cent sulphuric acid and dried at 60°C .; Fibre 2 was treated with $\frac{1}{2}$ per cent hydrochloric acid and dried at the same temperature; and Fibre 3 with $\frac{1}{2}$ per cent acetic acid. The curve shows that the latter thread has suffered least. (See also pages 55-56.)

Curves, Fig. 20, show the behaviour of an over-bleached artificial silk thread (1), compared with a normal thread (2). The abnormal behaviour of the fibres injuriously affected by chemicals, compared with that of normal fibres, which continues even on repeated swelling, renders it possible to detect such faults even in the finished fabric, particularly if threads which have not been damaged in this way are present. This matter is frequently of importance, as such injured threads are greatly changed in dyeing properties, apart from their considerably decreased strength.

Other important indications can be obtained by Weltzien's method. We have already seen that the differences in the mechanical strains on the half-formed fibres before they reach the winding mechanism are the main causes for the varying degree of the adsorptive power for dyestuffs of artificial silk

* The following interesting communications on this subject may be mentioned: Wiederkehr, *Melliands Textilberichte*, 7, 41 (1926); P. Kraus, G. Krauter and H. Vollprecht, *Leipzig. Mschr. f. Textilind.*, 41, 404 (1926); H. Vollprecht, *Leipzig. Mschr. f. Textilind.*, 41, part 12 (1926); *Textile Forschung*, 8, 93, 98 (1926).

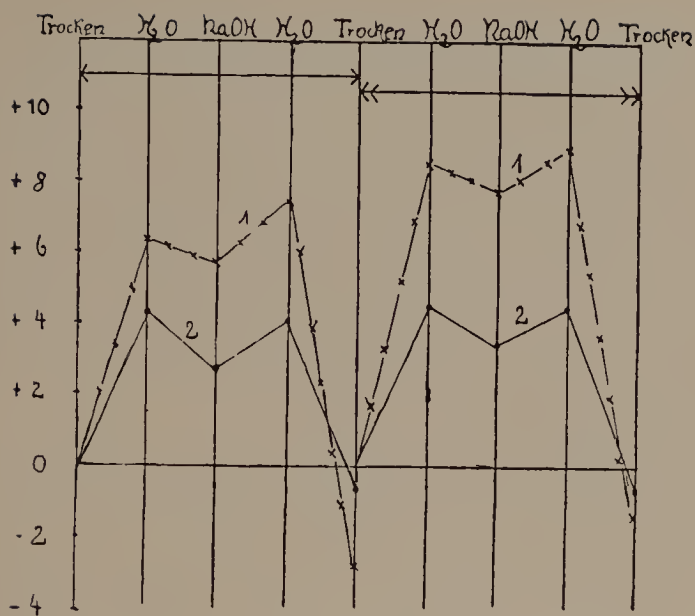


FIG. 20

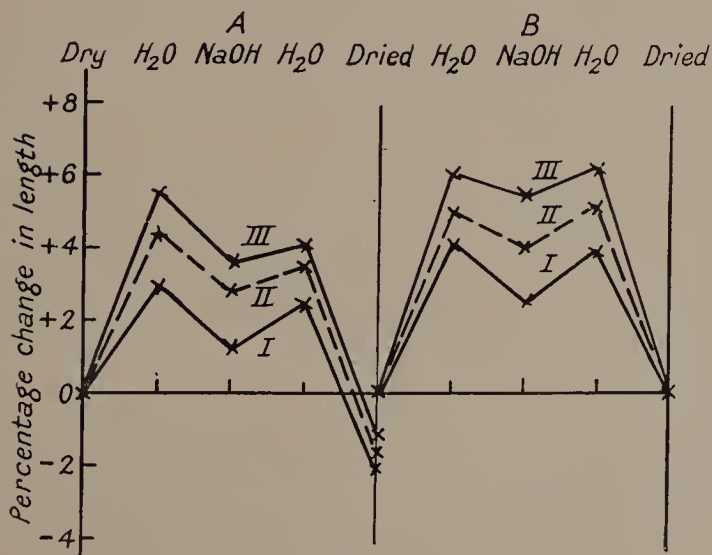


FIG. 21

threads of the same origin. Lehner and Jäger* have shown that the varying speeds of withdrawal may also cause varying tension on the thread. Littman and the author also investigated by Weltzien's method such threads which had been prepared by the author years before under conditions otherwise exactly similar. Fig. 21 shows that such threads show definite differences in swelling power, and that the mechanical strain of half-finished threads, in distinction to that of finished threads, cannot be removed by swelling in caustic soda solution. Thread I was produced at double the speed of withdrawal of thread III; the speed of withdrawal of thread II was intermediate between these.

Other things being equal, the swelling capacity and the adsorptive power for substantive dyestuffs decrease with increased mechanical stress of the half-finished thread during its manufacture.

The great value of Weltzien's method has been demonstrated. Weltzien† has also investigated the dependence of the degree of swelling of viscose and cuprammonium silks on the concentration of the sodium hydroxide solution. He found a similar relationship to that found by the author in the case of sulphite pulp and cotton.‡ For these substances, the author found a maximum swelling in 2.75 N. sodium hydroxide solution. Weltzien finds a more strongly developed maximum amount of swelling for cuprammonium silk with 3 N. NaOH, with a weight increase of 800 per cent; he finds a similar marked maximum for viscose silk in about 2.75 N. NaOH, with a weight increase of more than 500 per cent. In the case of wood pulp, the author found a marked dependence of the swelling power on the temperature, which is no doubt partially due to the lesser amount of liquid held between the fibres by

* Loc. cit. and W. Weltzien, loc. cit.

† Loc. cit.

‡ O. Faust, *Zellulose-Chemie*, 7, 153, 155 (1926). With regard to the dependence of the degree of swelling on the ratio of the weight of solid m , to the weight of swelling liquid p determined by Wolfram Ostwald, see W. Ostwald and R. Köhler, *Kolloid-Zts.*, 43, 233 (1927); when p becomes infinite, that is, when $\frac{m}{p} = 0$ the greatest degree of swelling occurs, according to Ostwald. See also P. N. Pawlow, *Kolloid-Zts.*, 44, 44 (1928).

capillary action at higher temperatures. In the case of artificial silk at higher temperatures of 80° to 100° C., no decrease of the tensile strength when wet compared with that at the ordinary temperature occurred ; on the contrary, the change was scarcely perceptible, or, at most, positive, from which one may conclude that the swelling power is slightly lessened at higher temperatures. In any case, however, in such investigations great attention should undoubtedly be paid to the maintenance of a constant temperature.

CHAPTER VII

THE CHEMICAL INVESTIGATION OF ARTIFICIAL SILK

IN practice, chemical investigations of artificial silk are only carried out in exceptional cases. They are confined to the usual determinations, well known in the case of cellulose,* excepting in so far as impurities are determined, such as iron or other metals, or possibly gypsum, and so forth. These are determined in the usual manner, and their qualitative detection may advantageously be effected by the usual micro-chemical methods.

Apart from the methods described in the last chapter, overbleaching can be detected by greater dyeing power, and over-treatment with acid by decreased dyeing power. The latter method is more advantageous than the former, more particularly if individual areas have been attacked, as in the case of spurting. Certain precautions must, however, be observed; for example, the copper ratios determined on artificial silk are somewhat uncertain.† We give below a table prepared by the author, together with E. Graumann, on the determination of copper ratios of artificial silk fibres of various origin, which point to certain differences which are, however, of no practical

TABLE III
COPPER RATIOS AND VARYING DEGREES OF HYDROLYSIS OF VARIOUS
ARTIFICIAL SILK FIBRES

Method of Investigation	Travis Silk	Elsterberg	Emmenbrücke	Elberfeld	Küttner	Bem-berg	Köln-Rottweil	
							Vistra	Vistra
Reduced copper	—	2.89	2.68	2.92	3.64	2.12	3.23	3.27
Hydrated copper	—	1.21	0.52	0.19	0.91	1.88	2.35	2.41
Corrected copper ratio	1.40 %	1.68	2.16	2.73	2.73	0.24	0.88	0.86
Hydrolyzation difference	16.07 %	11.13	11.34	12.40	12.49	13.27	14.91	13.40
Titre of individual fibre	—	6.2	5.8	7.4	7.3	1.4	3.4	1.2

* Schwalbe and Sieber, *Die Chemische Betriebskontrolle in der Zellstoff- und Papierindustrie* (Berlin, J. Springer).

† M. Freiburger, *Zts. f. angew. Chem.*, 30, 121 (1917); C. G. Schwalbe, *Zts. f. angew. Chem.*, 27, 567 (1914).

importance. They do not generally suffice for the distinction between these various forms of artificial silk, for which purpose, moreover, much better physical and physico-chemical methods have already been described.

In the table, the hydrolyzation differences are also given, that is, the copper ratios, which are found after 2 to 3 gm. of air-dried material have been hydrolyzed by boiling with 5 per cent sulphuric acid for 15 minutes, with stirring.

We wish to refer specially to the investigations recently carried out by Karrer* and his co-workers, H. Illing, P. Schubert and H. Wehrli, on the enzymatic degradation of cellulose hydrate under the action of the cellulose of the edible snail. These investigations may possibly yield further information on the micro-structure of artificial silk, and may also possibly enable artificial silks of a certain type to be distinguished, such as viscose silk produced by the Müller patent, German patent 187,974, and more particularly according to German patent 287,955/296 of the Vereinigte Glanzstoffabriken, Elberfeld, which is now produced by all viscose silk works throughout the world. A distinction between these silks, according to their method of manufacture, is hardly possible by a determination of the cross-section and physical constants. Microscopic investigation, which is so valuable in other cases, also fails in this case, as in the special cases referred to in Fig. 21, in which the cross-sections are absolutely identical, whilst investigation of the swelling properties shows a clear distinction. In the products of the processes described in German patent 390,139 and German registered design 970,459, which may be identical in their chemical characters, the microscopic test fails, whilst apart from investigation of the swelling power and the varying behaviour towards dyestuffs, investigation of the stability towards enzymes renders a clear distinction possible in this case.† At the same time we wish

* P. Karrer, *Zts. f. angew. Chem.*, 37, 1003 (1924); *Zsigmondy-Festschrift, Kolloid-Zts.*, 36, 91 (1925); *Helv. chim. Acta.*, 8, 245, 797 (1925), *Melliands Textilberichte*, 7, 23 (1926); P. Karrer, P. Schubert and W. Wehrli, *ibid.* 8, 777 (1925); also P. Karrer and P. Schubert, *Helv. chim. Acta*, 9, 893 (1926); 10, 430 (1927).

† O. Faust, P. Karrer, and P. Schubert, *Helv. chim. Acta*, 11, 231 (1928).

once more to emphasize the importance of the use of the microscope, and especially of the polarization microscope, for distinguishing artificial silks. Chemical methods of investigation are almost exclusively confined to the determination of the kind of silk (cuprammonium, viscose, nitrate or acetate silk), and seldom throw light on the quality, which can be much better determined by physical methods. Chemical investigations only become of importance, together with physical methods, in case of dispute as to whether a silk has been damaged by over-bleaching, acid treatment, and similar influences during its conversion into fabric.

W. Weltzien* found, during investigation of the solubility of numerous artificial silk samples in sodium hydroxide solution of various concentrations, that all such silks show a maximum solubility in a solution containing 10 gm. of NaOH per 100 c.c. of the solution. This solubility is 100 per cent for nitrate silk, 40 to 50 per cent for viscose silk, and 31 per cent only for cuprammonium silk. In the case of viscose silk, the solubilities of fibres of low titre are greater than those of higher titre. Earlier and unpublished investigations on viscose silk by the author yielded similar results to those found by Weltzien. According to Weltzien's results it appears possible to distinguish the various varieties of silk by chemical means.

In consequence of the nitrate groups which are always present in very small amount, nitrate silk gives the well-known dark blue coloration with diphenylamine and sulphuric acid, which constitutes a reliable distinction between this and all other varieties of artificial silk.

The ash of cuprammonium silk always contains traces of copper which may be chemically detected, but it must be remembered that this element also sometimes occurs in viscose silk, in which case it has its origin in the apparatus. Even an ultra-microscopic investigation does not enable one to distinguish between cuprammonium and viscose silk with absolute certainty.† However, the somewhat opaline, fish-like lustre

* *Papierfabrikant*, 25, 66 (1927).

† A. Herzog, *Die mikroskopische Untersuchung der Seide* (J. Springer, Berlin, 1924), p. 82.

of cuprammonium silk is a characteristic which definitely distinguishes it for the specialist. Moreover, the cuprammonium silk at present sold can be distinguished by the fineness of its fibre, its almost circular cross-section, and its favourable physical constants. The adsorptive power for substantive dyestuffs of cuprammonium silk is greater and the depth of shade produced is darker than with all other silks, other things being equal.

Acetate silk can easily be distinguished from other silks by its solubility in organic solvents, and, moreover, on burning it with a match it forms bubble-like swellings similar to those produced with unweighted natural silk. The sensitiveness of acetate silk to such temperatures as are necessarily attained, for example, by ironing, has already been referred to. It is also readily distinguishable by its smell on burning. When treated irrationally, for example, with caustic alkalis, it may undergo saponification with formation of ordinary cellulose hydrate. Such a material resembles nitrate silk most closely in cross-section, but does not, of course, show the diphenylamine-sulphuric acid reaction. Its other properties are similar to those of a viscose silk of medium quality.

The above described distinctive properties of the various artificial silks will usually suffice for the specialist. We may, however, briefly refer to a few colour reactions which have recently been discovered.

According to K. Götze,* viscose silk is coloured brown by ammoniacal silver nitrate solution, whilst cuprammonium silk remains uncoloured. According to Rhodes,† the following solution is used for this test: 1 per cent AgNO_3 , 4 per cent $\text{Na}_2\text{S}_2\text{O}_3$, and 4 per cent NaOH solutions are mixed and boiled, and the silk is immersed for one minute in the boiling solution. The reaction also occurs, however, in presence of oxy-cellulose, which may have been produced by over-bleaching.

H. Sommer‡ refers to the ultramicro-structure investigated by A. Herzog§ to which we have already referred, and also to

* K. Götze, *Melliands Textilberichte*, 6, Part 10 (1925).

† *Leipz. Mschr. f. Textilind.*, 41, Part 5 (1926).

‡ *Zts. f. d. ges. Textilind.*, 30, 126 (1927).

§ Loc. cit. and *Textile Forschung* (1921), Part 1.

the differences in cross-section ; also to the results of A. Lehne,* and describes the following colour reactions—

Reagent	Coloration with Cuprammonium Silk	Coloration with Viscose Silk
Methylene Blue	Weak	Strong
Congo Red	"	"
Solamine Blue F.F. (Agfa), 1 per cent solution	"	"
Naphthylamine Blue 4 B (Cassella), hot neutral bath	Dark blue	Light blue
Benzo Pure Blue (Bayer)	Dark	Light
Oxydianiline Black A (Cassella)	"	"
Congo Brown G (Agfa)	"	"
Ruthenium Red (Beltzer)	Very weak	Definitely pink
Fuchsine Sulphuric Acid (Herzog)	Almost colour- less	Reddish to red
Schwalbe's zinc chloride-iodine solu- tion, applied for a few moments and the fibre well rinsed	Weak	Strong

W. Wagner† recommends the following solution as a distinctive reagent: 4 gram. of sodium ammonium phosphate + 1 gram. sodium carbonate + 25 c.c. water are warmed with a solution of 5 gm. Pierccarmine (Ranvier)—(as supplied by E. Merck, Darmstadt, or Dr. G. Grübler & Co., Leipzig)—in 75 c.c. water, the sample turned for 10 minutes in the cold solution, and then well washed. Cuprammonium silk acquires a dark pink to wine red colour and viscose silk a light pink colour. A 1 per cent weakly ammoniacal solution of carminic acid is also recommended for distinguishing these two varieties of silk.

All these colour reactions, which are mainly concerned with different depths of the same shade only, must be used with a certain degree of discretion, and are probably only of value in the hands of an experienced specialist. The examination of a cross-section, which can usually be prepared and diagnosed by

* *Zts. f. d. Ges. Textilind* (1922), No. 47.

† *Melliands Textilberichte*, 9, 246, 367 (1927).

a practised hand in a few minutes with the simplest implements, generally yields a quicker and more certain result.*

* We may also refer here to the very complete investigations of W. Weltzien and K. Götze (*Die Seide*, 32, 401 (1907)), who determined the capillary rise of 132 solutions of substantive dyestuffs in various viscose silks of fibre titre 1, 2·7, 6·6, and 8·1, and in cuprammonium silk. They found that 56·8 per cent of the dyestuffs rose to a higher point in the same time (up to 60 minutes) in viscose silk than in cuprammonium silk. They recommend, as specially suitable for distinguishing between viscose and cuprammonium silk, Brilliant Benzole Blue, 6 B. The differences are greater when working at a higher temperature, but are noticeable even at the ordinary temperature and are, of course, due to the differing colloidal structure of the cellulose gels produced by the two processes.

PART II. TECHNICAL SECTION

CHAPTER VIII

RAW MATERIALS*

THE machinery for the manufacture of artificial silk is largely the same for all processes, as the purpose to be achieved is always the same, namely, to draw out spinning solutions to fine threads. For this reason one and the same apparatus may be used for all processes except in special cases, which are largely determined by purely chemical considerations.

Wood Pulp. As already mentioned, sulphite wood pulp can be used in many cases for the manufacture of artificial silk, and is used almost exclusively for viscose silk. For the manufacture of cuprammonium silk, nitrate silk and acetate silk, cotton and linters (the waste of short-fibre residues chemically identical with cotton, which adhere to the cotton seed after the removal of the cotton) are almost exclusively used. However, the development of these branches of manufacture has largely reached the stage at which they are almost prepared for the use of wood pulp, the main necessity being the uniformity of the latter, more particularly with regard to the viscosity of the solutions prepared from it. This uniformity is now achieved by many works; thus, for example, Zellstoffabrik Waldhof, Mannheim-Waldhof, has for many years prepared an excellent special wood pulp for the manufacture of artificial silk, which is equal to all requirements regarding uniformity of the viscosity of the solutions and chemical reactivity.

In this connection we may refer to the process of E. Opfermann,† who subjects the wood pulp to an alkaline bleach before

* The illustrations of apparatus and machinery accompanying the following descriptions and the list of names of the firms who were good enough to place these at the author's disposal are in no way complete, and have merely the object of enabling the reader to form a general idea of the machinery in question.

† German patent 436,804, VII, 55c.

the final processes of manufacture. E. Belani* describes the utilization of Pomilio cellulose for the manufacture of artificial silk; this is a fibre produced from esparto by decomposition with gaseous chlorine.† According to Belani's account this process seems to be satisfactory, but would presumably only be used in special areas in which no wood is available but only varieties of grass, possibly bamboo.

It is alleged that in America cellulose prepared from straw has been used with success for the production of artificial silk.‡

The requirements of various works, regarding the quality of the wood pulp which they use, vary, more particularly regarding the viscosity, but the requirements with regard to uniformity also vary; they are, however, quite rightly very high, and it would be interesting to follow the manner in which the large wood pulp works have succeeded from year to year in meeting these increased requirements. Friendly co-operation would certainly lead to further successes.

Apart from uniformity of the viscosity, which is regulated by concentration of the boiling liquor and the duration, pressure and temperature of the boiling process is subsequently adjusted during the bleaching process, and, in the case of viscose manufacture, by regulation of the ripening period and ripening temperature of the alkali cellulose, the proportion of so-called α -cellulose in the wood pulp is of fundamental importance.§ α -cellulose is that portion of the pulp which is insoluble in sodium hydroxide solution of 17.5 to 18 per cent. According to Hottenroth|| a good wood pulp for artificial silk contains 89 to 90 per cent of α -cellulose. H. Bubeck¶ proposes to determine the proportion of α -cellulose by diluting the 18 per cent caustic soda solution with which the wood pulp has been

* *Leipz. Mschr. f. Textilind.*, 43, 390 (1927).

† See also H. Wenzl, *Papierfabrikant*, and H. Wenzl, *Zellstoffherzeugung mit Chlor*. (G. Bornträger, Berlin, 1927).

‡ *Chemikerzeitung*, 51, 280 (1927).

§ H. Jentgen, *Laboratoriumsbuch für die Kunstseide und Ersatzfaserindustrie* (Halle, 1923); C. G. Schwalbe and R. Sieber, *Die chem. Betriebskontrolle in der Zellstoff- und Papierindustrie*, 2nd Edition (1922), pp. 221–222.

|| V. Hottenroth, *Die Kunstseide* (Leipzig, 1926), pp. 71, 304.

¶ *Der Papierfabrikant*, 34 (Special Number), 66 (1926).

mercerized to about 9 to 10 per cent by the addition of water or dilute caustic soda. The degree of swelling of cellulose is at a maximum* in caustic alkali of this concentration, and its solubility is at a minimum†; appreciably more non-cellulosic ingredients which may, however, be a form of cellulose‡ of lower micellar magnitude (about 1 to 2 per cent in quantity), are dissolved and are removed by washing with caustic alkali and finally with water.§

The portions of the pulp dissolved by this procedure, namely, the so-called “ β -cellulose” (the portion which can be precipitated by acid from its alkaline solution), and “ γ -cellulose” (the portion not precipitated by acids), are largely dissolved during the conversion of the pulp into artificial silk and thus lead to an equivalent loss of yield. It should be noted, however, that during manufacture the cellulose itself is partially decomposed, so that finished artificial silk always contains a variable

* O. Faust, *Zellulosechemie*, 7, 153, 155 (1926); see also P. N. Pawlow, *Kolloid-Zts.*, 44, 44 (1928).

† J. D’Ans and A. Jäger, *Zellulosechemie*, 6, 137 (1925). These authors also propose to utilize caustic alkali solution of the greatest solvent power for the investigation of wood pulp; that is, for the determination of α -cellulose.

‡ See also G. Porrvik, loc. cit. 137, Tables 21 to 24.

§ The determination of α -cellulose is at present always carried out by Jentgen’s method with caustic soda solution of 18 per cent by weight. By this method, however, various investigators obtained results differing by several per cent, and this is the case to a still greater extent when caustic alkali solution of 9 to 10 per cent by weight is used. We may, therefore, refer here to the interesting and important investigations of Wolfram Ostwald and his co-workers, which culminate in the so-called “solid phase” law (W. Ostwald, *Kolloid-Zts.*, 41, 163 (1927)); this law states that in the case of colloids in general the proportion which goes into solution is not—as in the case of solutions of crystalloids—dependent of the quantity of solid substance present. The solubility is at a maximum for a perfectly definite relation of solvent to solid phase, which depends on the concentration of the solvent, for example, in the case of solutions of alkalis, acids or salts. W. v. Neuenstein (*Kolloid-Zts.*, 43, 241 (1927)) finds that for sulphite pulp (Hösch), for example, in 9.4 per cent sodium hydroxide solution, this maximum occurs with a proportion of 6.5 gm. of pulp to 20 c.c. of solution, that is, with a comparatively small amount of the latter. The changes of solubility when these proportions are altered are quite considerable. W. Ostwald has confirmed this law in the course of many investigations with various substances (see *Kolloid-Zts.*, 43, November No., 1927), and has also published a detailed theoretical explanation of the various cases (*Kolloid-Zts.*, 43, 249 (1927)). See also A. v. Buzágh, *Kolloid-Zts.*, 41, 169 (1927), and 43, 216 (1927); also E. v. Mühlendahl and J. Reitstötter (*Kunststoffe*, 1927, No. 7), who found that similar relations held for solutions of cellulose nitrate in alcohol. With regard to the determination of α -cellulose, see also G. Porrvik, *Papierfabrikant*, 26, 81, 120 and 133 (1928).

amount of material soluble in alkali.* The reasons why the proportion soluble in alkali of wood pulp for artificial silk manufacture should not be too high, are not only economic but also technical. It has been found, however, that the recently marketed so-called " α -cellulose," containing about 94 per cent of material insoluble in alkali,† offers no advantages, particularly if its high price is taken into consideration.

In estimating the value of a wood pulp, its capability of swelling is of a certain, although not predominant, importance. It is investigated, for example, by determining how many times its own weight of liquid are adsorbed by a weighed quantity of wood pulp sheet after dipping in mercerizing liquor (18 per cent NaOH solution), the material being then allowed to drain and weighed. The determination of the well-known copper ratio, according to C. G. Schwalbe‡ is of undoubted value in so far as the hydrate copper—that is, the amount of copper adsorbed from Fehling solution without reduction to cuprous oxide—is concerned. This ratio increases with the swelling power of the material under investigation. The true copper ratio§—the so-called "reduced" copper, which was introduced by Schwalbe—is undoubtedly of value for determining the quality of wood pulp. According to Hottenroth,|| it should be between 2 and 3 per cent, and is still less in the case of the above-mentioned α -celluloses. This determination by Schwalbe's method, particularly in the modified form described by Hägglund,¶ is now generally used in the artificial silk and wood pulp industries, and is to be preferred to the method described by Braid,* which requires a longer time and gives values which differentiate the various wood pulps less definitely. Hägglund's modification is carried out as follows: The reduced cuprous oxide is determined by treatment with a solution of a ferric

* See also W. Weltzien, *Papierfabrikant*, 36, 66 (1927); *Ber.*, 60, 2024 (1927) and *Die Seide*, 32, 371 (1927); also P. Waentig, *Ber.*, 60, 112 (1927).

† G. A. Richter and Molton O. Schur, U.S. patent 1,643,355, assigned to the Brown Co. (French patent 621,412).

‡ C. G. Schwalbe and R. Sieber, loc. cit., p. 242.

§ C. G. Schwalbe, *Chemie der Zellulose* (Berlin, 1911), pp. 625–629; see also Schwalbe and Sieber, p. 230.

|| V. Hottenroth, loc. cit., p. 71.

¶ See Jentgen, loc. cit., p. 43; E. Hägglund, *Papierfabrikant*, 17, 301 (1919).

** *Rev. gén. color.*, 25, 35 (1921); *Zellulosechemie*, 5, 99 (1924).

salt and titration of the ferrous salt so formed with permanganate solution.

All the above-mentioned methods of investigation are valuable and are in general use, but a complete valuation of a wood pulp is only possible by studying its behaviour under practical conditions.

The Other Raw Materials: Water. The other raw materials required for the manufacture of artificial silk are generally supplied by the heavy chemical industry of a satisfactory degree of purity. With regard to their investigation, we must refer to Jentgen's Laboratory Manual, to which we have frequently made reference. In the case of caustic soda solution it is particularly important that the contents of carbonate and other salts, and more particularly of chloride, should be low. These two impurities are, however, only present to a small and harmless amount in the concentrated 38 per cent caustic liquors supplied in tanks by the industry, on account of their low solubility in such a liquid. Traces of iron in the caustic liquor, which are strongly absorbed by wood pulp, are mainly due to rust in the tanks, and can be reduced to a sufficiently low figure by allowing to settle.

The degree of purity of the water is particularly important, and Jentgen gives exact data on this matter.* The quality and quantity of the available water is a vital matter for an artificial silk works, and for the possibility of a large output; the facilities for disposal of the effluents, contaminated by the necessary quantities of acid, and so forth, is of equal importance. The removal of mechanical suspensions by filtration is essential, particularly when river water is used. Also the water must, of course, contain no materials which might stain the silk, such, for example, as the humin substances contained in water from moorlands. The degree of hardness, that is, the contents of carbonates and sulphates of calcium and magnesium, should be as small as possible, and must, if necessary, be reduced in a special permutite plant by treatment with an artificial sodium aluminium silicate, by which means the calcium or magnesium is replaced by sodium. The permutite mass can be regenerated

* H. Jentgen, loc. cit.

by treatment with sodium chloride solution and subsequent washing with water. Finally, the iron content of the available water plays an important part, as when the finished fibre comes into contact with water containing iron, this latter is deposited on the fibre, causing a yellowish tint which cannot be removed. The iron can be easily and rapidly determined by colorimetric methods. Regarding the investigation of water in general, we may refer to the above-mentioned book by Jentgen,* and also to that by Tillmans.†

The manufacture of the spinning solutions naturally varies according to the chemical process used, and must be dealt with specially.

* H. Jentgen, loc. cit.

† J. Tillmans, *Die chemische Untersuchung von Wasser und-Abwasser* (Wilh. Knapp, Halle a. S.).

CHAPTER IX

DRYING AND FILTRATION

Drying. Before treatment the wood pulp or cotton must be dried and the moisture reduced to 4 to 5 per cent. Excepting when the wood pulp is supplied in the form of sheets of considerable size, it may advantageously be dried in large drying chambers such as those supplied by E. Bernhardt, Leisnig, Saxony. These chambers are about 6 metres high and 2 metres wide, and the disintegrated cellulose or cotton is introduced at the top on an endless sieve which travels along a sinuous path along seven parallel tracks from top to bottom. During its passage the cellulose is heated from below by a current of air which is warmed by steam-heated radiators. Such an apparatus may, for example, have an output of 1500 to 2000 kg. of pulp per 24 hours. The passage of the wood pulp through the chamber requires about half an hour. The dried pulp falls out below and is carried to the treatment shed by a pipe system with fans.

If, however, the cellulose is to be used in the form of sheets, as is now generally the case since the successful introduction of the Häusser dipping press, it must be dried in larger chambers, or a so-called tunnel drying oven is used, such as is manufactured, for example, by the Maschinenfabrik Friedrich Haas, Lennep, Rhineland. Such a drying chamber is shown in Fig. 21A. These drying chambers are also supplied for a large output in two storeys, with a suitable antechamber. The wood pulp sheets are suspended from a chain conveyor, carried upwards and passed through the upper compartment of the drying chamber in one direction and return through the lower compartment, from which they are removed in a dry state. A uniform stream of uniformly heated air is passed through the drying chamber in counter-current to the wood pulp, being driven by fans, and drying is thus effected.

These drying chambers require a relatively small amount of

power, and are particularly suitable for the purpose, as the temperature never attains more than a maximum which is readily adjustable. We may also refer here to the drying machinery of Benno Schilde, Maschinenbau A.G., Hersfeld:

Filtration. Owing to the circumstances that the spinning solution has to be extruded through very fine apertures during spinning, it must be subjected to a very careful filtration before entering the nozzles. Apart from the careful production of the spinning solution from a chemical standpoint, filtration must be considered as an extremely important measure in order to

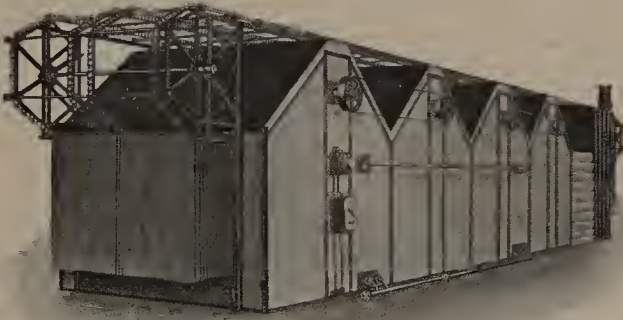


FIG. 21A

ensure satisfactory spinning. Partial blockage of the spinning apertures leads to the production of bad (lousy) silk, or if individual spinning apertures are completely blocked, to an alteration of the count of the individual fibres of the thread, as equal quantities of spinning solution are always driven through the nozzle in equal time, owing to the action of the spinning pumps.

A thread produced by a partially blocked nozzle maintains the desired total titre in consequence of the action of the pump, but in consequence of their reduction in number the individual fibres have a higher titre than would be the case were the nozzle clear, and, consequently, the whole thread has a different appearance and smaller covering power. More particularly, it has a greater adsorptive capacity for dyestuffs in consequence of its greater individual titre, and this alteration is very

noticeable in the finished fabric. It is impossible, therefore, to devote too much attention to filtration.

Frame filter presses, such as are otherwise used in the chemical industry, are in general use for filtration.

The spinning solutions are repeatedly filtered; first, after they have been adjusted, and during their passage to the solution tank, and again during their passage from the solution tank to the machine. At both these points frame filter presses are introduced which are charged with layers of cotton wool. In order to prevent cotton wool fibres from being carried away with the solution, the frames are fitted with filter cloth, usually of nettle cloth and with fine muslin,* at any rate on the side directed towards the spinning machine.

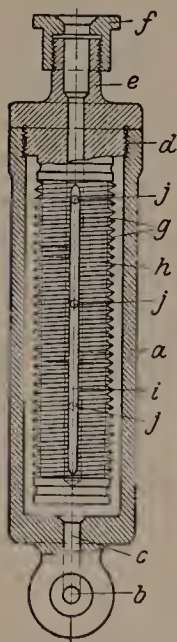


FIG. 22
FILTERING
CANDLE

Per 10 square metres of filtering area, about 15,000 to 20,000 litres of spinning solution can be filtered in 24 working hours, the amount varying according to the viscosity of the solution, which varies with the different processes. The cotton wool filtering layer is used of such a thickness that it weighs about 250 grammes per square metre. In the wet spinning process the filtration pressure is 3 to 4 atmospheres; too high a pressure is not desirable. In the dry spinning process, for which highly viscous solutions are necessary, much higher pressures must naturally be used, and the whole apparatus is designed to meet this requirement.

In order to prevent impurities from the piping from entering the spinning nozzles in spite of the filtration, a so-called "filtering candle" is inserted before the nozzle. Fig. 22 shows a section of such a nozzle according to W. P. Dreaper, London.†

a is an outer casing of suitable material, such as ebonite, of sufficient strength to withstand the pressure at which the

* In the filtration of spinning solutions for the production of cuprammonium silk, very fine metallic sieves, for example, of nickel, must be used for filtration in consequence of the gelatinizing and dissolving properties of the solution.

† German patent 414,675/29a.

solution is filtered. If necessary an auxiliary valve can be attached to the filter, so that the pressure may not exceed a definite amount, or the outer casing *a* can be suitably reinforced. This outer casing *a* is provided with a swivel-joint *b* through which the solution enters at *c*. The casing *a* is connected at *d* by means of a screw-joint or otherwise, through an attachment *e* and glass delivery tube with the spinning nozzle ; the nozzle is connected with the glass tube by means of a screw-cap, and the glass delivery tube is connected with the filter at *e* by means of a similar cap *f*. The outer casing *a* can readily be removed from the spinning nozzle by unscrewing *f*, in order to clean it and to replace the filtering medium, which is attached or wound round the grooved surface of the candle *h*. The candle *h* is provided with an axial channel *i* with a number of lateral openings or connecting channels *j* through which the filtered solution passes into the central channel. A so-called "nozzle filter" is also inserted in front of the nozzle and consists of a wire gauze and a thin layer of muslin.

CHAPTER X

SPINNING APPARATUS

THE spinning apparatus is of similar character for all processes, in so far as its object is to extrude the spinning solution in a uniform manner through fine apertures and to collect the spinning mass, after its conversion into fibre form and simultaneous change to the gel condition, by a collecting device, causing a definite rate of withdrawal adjusted to the requirements of the process. Characteristic differences are associated with the so-called "wet" spinning and "dry" spinning processes. We will first briefly describe those features which are common to all processes.

Spinning Nozzles. The spinning nozzle is the contrivance which serves to produce the actual formed thread in a similar manner to the natural spinning apertures of the silkworm or spider, through which these latter expel their spinning solution; these are, therefore, the actual thread formers.

Nozzles may be divided into those with but one spinning aperture, such as were usual in the early stages of the manufacture of artificial silk, and those with many apertures. When spinning cellulose nitrate solutions by the dry spinning process, the wear on the nozzle is purely mechanical and not appreciably chemical. Glass tubes were ordinarily used, one end of which was everted to form a flange for the purpose of attachment, whilst the other end formed a capillary tube a few millimetres long and of accurately adjusted bore, of the order of 0.1 mm. In order to produce a uniform product, the same quantity of spinning solution must be expelled per unit of time from all the spinning apertures, the fibres from which are collected to form a thread. When single apertures were used it was necessary so to adjust the lengths of the capillaries that they fulfilled this condition, even although they varied slightly in bore; this, of course, entailed a considerable amount of trouble.

In the case of nozzles with several apertures, this possibility does not exist, and the greatest care must, therefore, be devoted not only to the absolute uniformity of the holes, but also to the absolutely uniform thickness of the nozzle wall ; all the nozzles must also be identical with regard to these dimensions. These requirements were most easily fulfilled by metallic nozzles. In the case of the viscose process, however, which is the most widely used, this metal has to fulfil stringent chemical conditions on account of the alkaline and sulphur-bearing character of viscose and the chemical activity of the spinning baths, which are frequently hot and acid. For this reason the large platinum firms, more particularly W. C. Heräus G.m.b.H., Hanau a.M., devoted themselves to the wholesale manufacture of such nozzles. Platinum was originally used, but being expensive was gradually replaced, first by gold-platinum alloys and then by the still cheaper gold-palladium alloys. Molybdenum nozzles have also been experimentally placed on to the market by the Siemens-Werke, Berlin-Siemensstadt.

Metallic nozzles offer the further advantage that they can rapidly be inspected in order to observe whether individual apertures in the cleaned nozzles are wholly or partially blocked, by a simple illuminating apparatus, such as is supplied by the Zeiss Works, Jena. This is possible in consequence of the small thickness of the nozzle plate, which is about 0.30 mm.

This advantage is shared by the porcelain nozzles which have recently been produced in great perfection by the porcelain works Hermsdorf A.-G., Hermsdorf i. Th. It is a remarkable fact that these nozzles possess great uniformity with regard to size of aperture and thickness of nozzle plate, which latter can be reduced to a few tenths of a millimetre. These thin nozzle plates are ingeniously strengthened by porcelain ribs, so that the nozzles, which show the well-known unexcelled chemical resistance of porcelain, also comply mechanically with the requirements of the manufacturing operations.

In order to control the aperture size, W. C. Heräus, Hanau, jointly with the optical firm of E. Leitz, Wetzlar, has introduced a microscopic nozzle-testing apparatus,* which is shown in

* For an exact description of this apparatus see *Die Kunstseide* (1927).

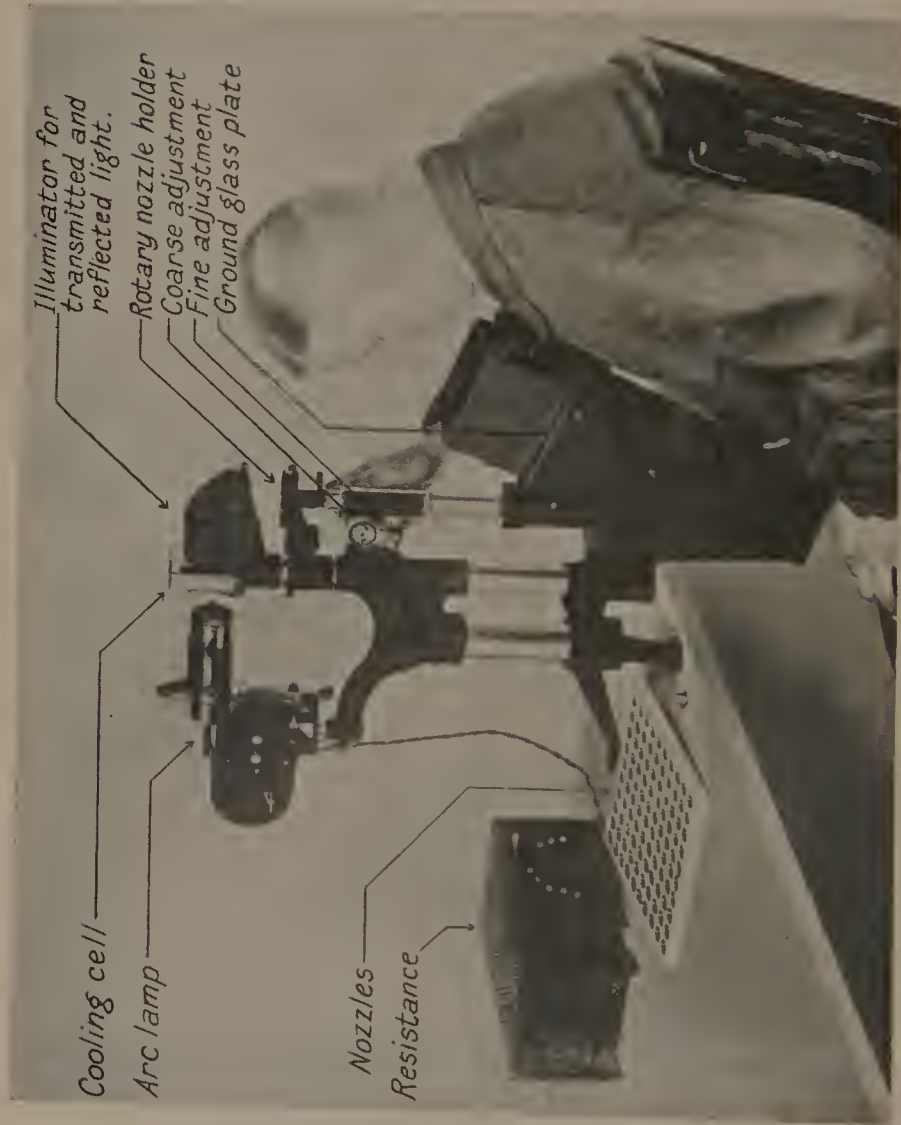


FIG. 23. USING NOZZLE TESTING APPARATUS

Fig. 23. The observer turns the nozzle holder with the loosely attached nozzle, and the apertures appear one by one on a ground glass disc at a magnification of 130 to 150, together with a graduated scale. Meanwhile, the exact adjustment can be effected by the use of one hand only. With a little practice, one man can check the width, evenness of circumference and cleanliness of 1000 apertures per hour. Very accurate glass nozzles, with many apertures, are produced by the glass-blowing firm of Paul Aschenbrenner, Nowawes, near Potsdam, Plantagenstrasse 10 ; similar nozzles are also produced by the firm of Geissler, Bonn, and are still much used, particularly in America.

Very many other materials have also been proposed for the manufacture of nozzles, but without success.

Copper nozzles with wide apertures of 1 mm. are, however, used for the cuprammonium stretch spinning process. They are very durable and cheap, and have the very great advantage that partial or total blockage of the apertures, which is so frequently the cause of the production of broken threads, need never occur.

The Dry Spinning Process. The liquids which may be used for the dry spinning process are solutions of cellulose nitrate, in ether-alcohol or other solvents, solutions of cellulose acetate in acetone or similar solvents, and possibly solutions of cellulose ethers* in volatile solvents. Apparatus for the purpose may take the form shown in Fig. 24, which is patented by the Soc. pour la Fabrication de la Soie "Rhodiaséta," Paris, in German patent 403,736/29A of 1924.

In the figure, 1 represents the cylindrical metallic wall of the chamber, which is composed of the suitably attached parts 1a and 1b ; the whole is held by a support, which is not shown ; 2 and 2a are the double walls between which a regulated supply of hot water is passed. This supply of hot water enters through the tubes 3, 3, and is discharged through the tubes 4, 4. The walls are also provided with lagging, 5, 5. The water supply may be arranged in series or in parallel. The thermometers 6, 6, arranged at various heights, indicate the temperature

* Still in the experimental stage.

inside the chamber. 7 represents the spinning contrivance with several nozzles, 7a, which revolves about an axis 9. The spinning solution enters through 10 after having passed through the filters, pumps, and so forth. 11 is

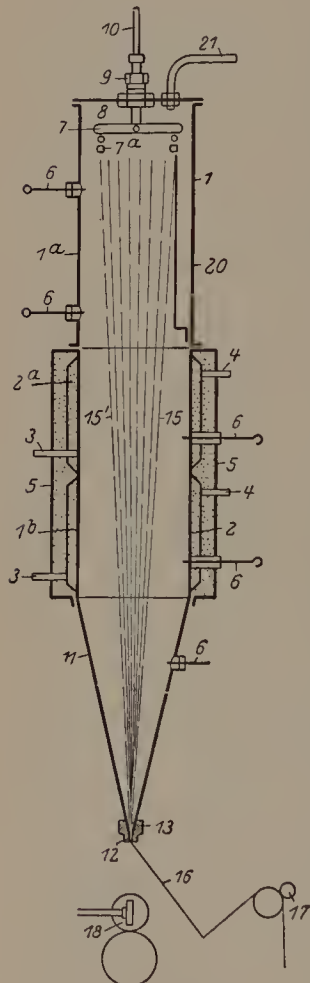


FIG. 24

DRY SPINNING UNIT

the conical metallic portion of the chamber—the funnel; the threads slide down the inner polished surface of this latter should they be ruptured. 12 is the discharge opening for the thread, and is drilled through two bronze fittings 13 attached to the end of the funnel. One of the bronze fittings 13 is movable, together with a gate in the conical portion. The broken lines 15, 15' represent individual fibres which unite to form a thread 16, which is conveyed to the farther parts of the machine by the contrivance 17. 18 is a pulley below the opening 12 which serves to wind the thread 16 should this be purposely or accidentally broken outside the chamber. The air which enters the cell through the thread outlet 12 becomes saturated with the vapours of the solvent and escapes to the top of the chamber at 21. Spinning may also naturally be carried out from below upwards. In that case the solvent vapours, which are always heavier than air, collect at that portion of the vessel at which the threads leave the nozzle, so that the rate of evaporation is considerably slower, in consequence of the saturation of the surrounding

air with the vapours of the solvent, than when spinning is carried out from above downwards as previously described. In order to avoid these difficulties various proposals have been made, for example, by Courtaulds, Ltd. (British patent 278,881 of 9/7/1927), and by the Nederlandsche Kunstzyldefabriek,

Arnhem, Holland (German patent application N.26,770, applied for on 30/12/1926) (Dutch priority 17/12/1926).

The spinning nozzles for the dry spinning process are usually constructed of glass, and both they and the rest of the apparatus must be able to withstand great pressures, as the solutions are very viscous. Pressures of 60 to 70 atmospheres are ordinarily used. In the dry spinning process, single aperture nozzles are still frequently used, as it is then possible to remove each individual fibre from the aperture when spinning has started and also to re-attach torn fibres. This implies a certain degree of complication, compared with the wet spinning process, but on the other hand it ensures that all the fibres are present in the finished thread, and that the formation of snarls is largely avoided. When the machine lies idle the individual apertures must be closed with small caps, so that the spinning solution may not solidify and obstruct the apertures.

Solvent Recovery. All dry spinning processes use volatile solvents. It is of the very greatest importance for economy in these processes that the solvent should be recovered as far as is at all possible. For this reason the dry spinning apparatus must be closed, as already described, and the vapours evolved from the fibres are aspirated into a suitable apparatus in which they are absorbed. In order to assist evaporation of the solvents, an arrangement for warming the spinning apparatus may be provided in the manner already described.

Ether-alcohol, which is mainly used in the production of nitrate silk, can be absorbed very completely by using concentrated sulphuric acid. This process has, however, certain disadvantages on account of the necessary reconcentration of the acid.

Recently a process has been proposed which was invented by Brégeat (French patents 502,882 and 502,957, Swiss patent 98,478/1921), according to which cresols are used as absorbents. Brégeat has also recently proposed the use of hydro-aromatic substances such as oil of turpentine, pinene, and so forth, which, however, are presumably hardly practical on account of their high price.*

* In this connection we may refer to the apparatus of Cheminova G.m.b.H., Berlin, S.W. 48.

The process of the *Farbenfabriken vorm. Friedrich Bayer & Co.*, Leverkusen, Cologne, using activated charcoal for adsorption, has proved particularly effective. The process is simple, very clean, reliable, and requires relatively little attention. We must also refer to adsorption by silica-gel, for which very effective apparatus is supplied by the firm of Borsig, Tegel.* This apparatus is, of course, suitable for use with any other solid absorption agents, possessing similar physical properties to silica-gel, and would presumably be suitable for use with activated charcoal.

Silica-gel is silica prepared by a special process, and being silica, it is extremely resistant to reagents and to temperature conditions. In appearance it resembles pure quartz sand, but has an exceptional ultramicroscopic porosity, by reason of which it is an exceptionally active absorption agent. If used in the granulated or finely ground condition it absorbs vapours of all kinds, which can usually be recovered by simple heating, and the gel is then ready for renewed use.

The Davison Chemical Co. and Silica-gel Corporation of Baltimore, have for years investigated the industrial uses of this material. Its behaviour towards various materials has been investigated by numerous laboratory experiments, on the basis of which apparatus for industrial plants has been designed, and such plants may now be considered to have been completely developed.

Two general types of apparatus may be used for the technical application of solid absorbents such as activated charcoal and silica-gel. The one type consists of several absorption chambers which work alternately, and in which the absorption agent is used in granular form, and is supported by sieves. In the other type the powdered absorption agent circulates in counter-current to the mixture of gas and vapour which is to be treated. In apparatus of the first kind losses cannot occur, whilst in

* Regarding solvent recovery, see also the excellent volume of I. L. Eekelt and O. Gassner, *Nitrocellulose, Campher, Pulver* (Leipzig, 1926, O. Spamer), pp. 142-156, which contains numerous numerical data and many diagrams and photographs of recovery plant in the cellulose nitrate industry, which may be satisfactorily applied to the industry of cellulose acetate. We may also refer to the excellent volume of H. Brunswig, *Das rauchlose Pulver* (W. de Gruyter, Berlin, 1926).

the second type of apparatus they are reduced to a very small amount of dust, which cannot be separated from the issuing gas by dust catchers. Silica-gel possesses the particularly valuable property of removing very small concentrations of

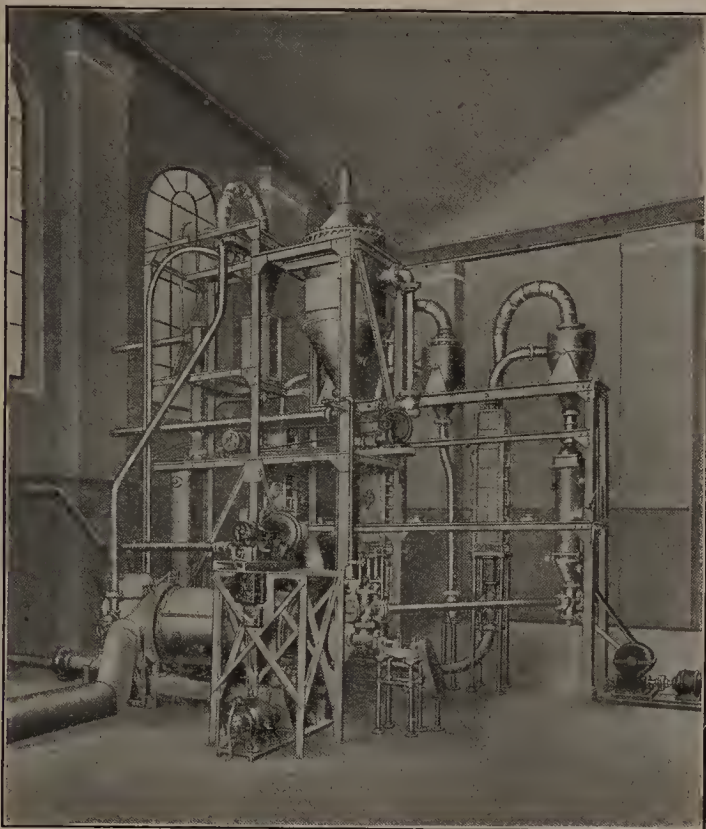


FIG. 25. SILICA-GEL ABSORPTION PLANT
(Borsig-Tegel)

vapours from gaseous mixtures, and it is also characterized by extremely low specific heat.

The firm of A. Borsig, G.m.b.H., Berlin-Tegel, together with Koks-Werken und Chemischen Fabriken A.-G., Berlin, and Chemischen Fabrik auf Aktien vorm. E. Schering, has acquired the exclusive rights for Germany and Eastern Europe to erect installations according to the patents of the Silica-Gel Corporation. Such an installation is shown in Fig. 25. It consists essentially of a system of tubes through which the gas containing the condensible vapours is driven by fans in counter-current

to a continuous stream of silica-gel. The system must be of such a length that the whole of the solvent is absorbed by the counter-current of silica-gel; in any given installation complete absorption is ensured by regulating the gas velocity on the one hand, and the velocity at which the silica-gel is passed in counter-current to the gas on the other.

The Wet Spinning Process. The methods of operation covered by the term "wet spinning process," may be divided into those in which solvents alone are removed by liquids, and those in which the spinning solution is chemically decomposed with simultaneous coagulation, frequently with immediate regeneration of cellulose hydrate. Apart from the cellulose acetate process, the mere removal of solvent is mainly practised in the cellulose nitrate and cellulose ether processes. In these cases, as in those described in the previous section, the recovery of the solvent plays an important part; otherwise the apparatus is more or less similar to that used in other wet spinning processes.

In the manufacture of artificial silk, three contrivances are in general use for winding the silk thread. These are (1) reeling machines, (2) bobbin machines, and (3) pot-spinning machines (centrifugal machines). We may also refer here to the continuous process of Boos.*

Reeling Machines. Reeling machines are mainly used for the manufacture of so-called "staple fibre," in which the principal requirement is the production of large quantities of fibre with a machine requiring as small a floor space as possible. Staple fibre is wound on to reels in the form of hanks, and from time to time these hanks are removed, either in continuous form by folding the reel together, or by cutting the hanks, which are then further treated. These hanks are then cut into small fibres, as far as possible of uniform length, which are further treated by the methods used in the textile industry for spinning cotton or waste silk. Fig. 26 shows such a machine, which is supplied by the firm of Carl Hamel A.-G., Schönan,

* J. J. Stöckly, "Forschungstätigkeit im Glanzstoffkonzern," *Textil-Echo*, 1925/26, No. 7, p. 173; see also German patents 235,134 and 259,816, of the Vereinigten Glanzstoffabriken, Elberfeld.

near Chemnitz. This single-fronted machine contains two sets of reels, so that when removing a full reel thread can still be wound on to the other. By the reciprocating movement of a bar, *B*, which carries the thread guides, between the spinning nozzles and the receiving reels, a greater or lesser degree of cross-winding of the threads on to the reel is ensured.

The machine shown contains 30 nozzles on each wing, these nozzles being 100 mm. apart. The thread is received from the

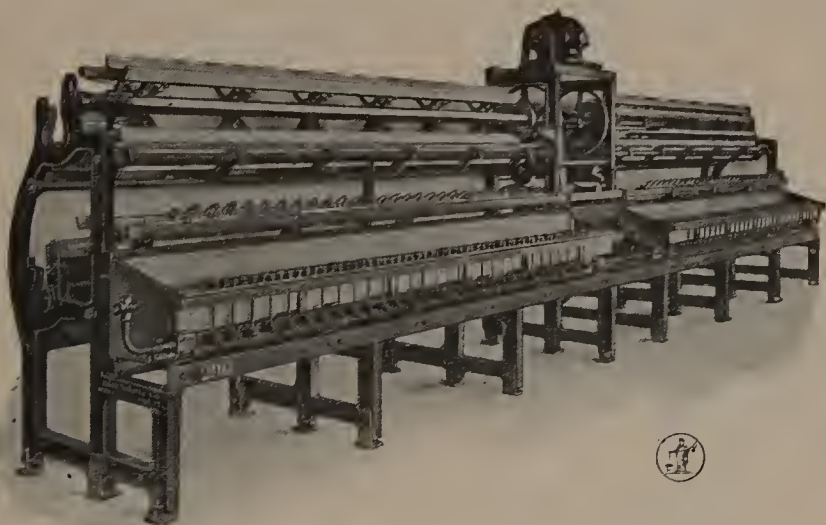


FIG. 26. STAPLE FIBRE SPINNING MACHINE
(Carl Hamel A.-G.)

back of the machine, and the drive is in the middle. (Regarding detailed arrangements of the spinning apparatus, see the following illustrations, more particularly Fig. 32.)

Another machine with so-called "independent reels," manufactured by the Düsseldorf-Ratinger Maschinen-und Apparatebau A.-G., Ratingen, is shown in Fig. 27. In this machine, each thread is spun on to an independent reel *A*, which enables the material to be removed in a compact form, with special ease. In this case, also, two reels are provided for each spinning nozzle *B*, so that they may be rapidly interchanged. As in all textile machines, the motion of the thread guides is controlled by means of the heart-shaped cam disc *D*. This disc turns eccentrically and drives a bar to which the thread guides

are rigidly attached. The motor drive is visible in the figure, and also the ventilating arrangements, the inlets *C* of which are frequently replaced by a continuous slot occupying the whole length of the machine. The main portion of the air-suction flue lies within the machine and is, therefore, invisible in the figure. In machines for the manufacture of staple fibre or thread from artificial silk waste, the ventilation is very important, as the large number of small threads evolve volatile decomposition products on leaving the precipitation bath,

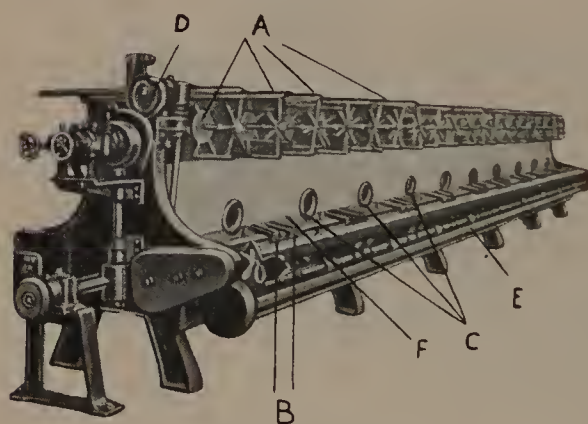


FIG. 27. DOUBLE-FRONTED MACHINE FOR SPINNING STAPLE FIBRE AND SCHAPPE
(Düsseldorf-Ratinger Maschinen-und Apparatebau A.-(G.)

which may seriously molest the operator, or even make it impossible for him to attend to the machine. Intensive ventilation of the machine is a hygienic requirement of the greatest importance, particularly in the spinning of staple fibre but also in that of artificial silk.

The supply of spinning solution passes through supply pipes *E*, which are situated on both sides of the machine. The precipitation bath *F*, which is best completely lined with lead, is provided with discharging pipes or weirs, and is also served by the ventilation inlets *C*, which are placed sufficiently far down for the purpose. All parts of the machine which come into contact with acid must be constructed of acid-proof material. The output of the machine naturally depends on the titre of the product. Normally, a schappe machine with 40 spinning nozzles produces 180 to 200 kg. of material of 1000 deniers per 24 hours. With finer counts the output of the machine in kilogrammes is reduced, and with lower counts it is increased.

Wool spinners also use this fibre in the manufacture of cheap clothing materials, more particularly such as are used in the

ready-made clothing trade ; the demand for the material for this purpose is increasing, and it is used partly admixed with wool and partly unmixed. The art of spinning is now so developed that staple fibre can be treated by all the methods used in spinning wool.

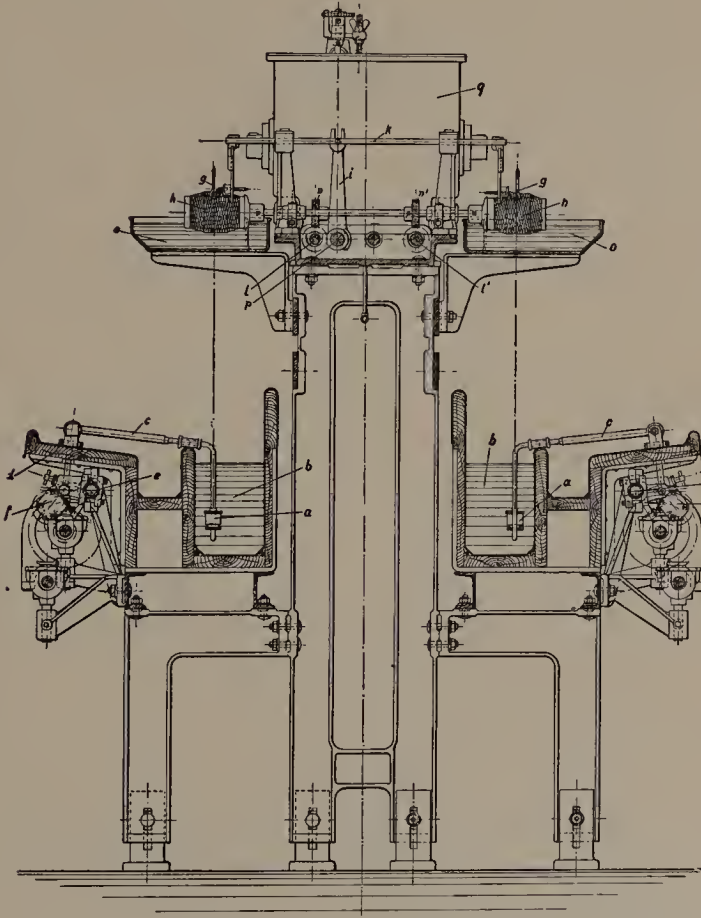


FIG. 28. ELEVATION OF DOUBLE-FRONTED ARTIFICIAL SILK SPINNING MACHINE
(Carl Hamel A.-G.)

Bobbin Spinning Machines. Bobbin spinning machines are mainly used for the production of threads of high counts. Such a machine of the newest type, constructed by the firm Carl Hamel A.-G., Schönau, near Chemnitz, is shown in sectional elevation in Fig. 28.

This figure shows the nozzles *a* in the spinning baths *b*.

In order to complete the filtration of the spinning solution, a filtering candle *c* is introduced into the supply system for the spinning solution. The machine is double-fronted. Below the trough-shaped tables *d*, supporting the spinning baths, there are situated the supply tubes for the spinning solution *e* and the spinning pumps *f* (see Figs. 7, 8, and 32), which ensure that each nozzle shall be uniformly supplied with spinning solution, with the object of producing a uniform thread. The thread passing from the nozzles and spinning bath is carried by the thread guide *g* to the rotary spinning bobbins *h*, on which it is cross-wound. For this purpose, the thread guide *g* is constrained to move reciprocally by means of the lever *i* and the bar *k*. The necessary movement is imparted by cam discs (see *d*, Fig. 27), which are contained in a closed box *q* and impart a reciprocating motion to the axle *p*, which in turn actuates the lever *i*. If necessary, a so-called "upper bath" *o* may be provided below the bobbins *h*. The bobbins are actuated by the shafts *l* and the gear-wheels *n* and *n'*.

The machine is provided with a contrivance by means of which the bobbins are automatically interchanged at definite and adjustable periods, so that they receive equal lengths of thread, and the operative has merely to displace the thread from the filled to the empty bobbin. Machines are constructed by the same firm in which this removal of the thread is also carried out automatically, by which means the requisite supervision is greatly facilitated and reduced.

Fig. 29 shows another machine of very practical construction, by Oscar Kohorn & Co., Chemnitz.

In this machine the swinging thread guides *A*, which are driven by cam discs, are of special interest. As the rate of withdrawal of the thread would otherwise be gradually increased as the bobbins are filled, in consequence of the increase in diameter of the spooled material, and as this would entail a reduction in the diameter of the thread were the supply from the spinning pumps to remain constant, conical pulley-drives *B* are used if the bobbins are to be heavily wound, by means of which the rate of rotation of the bobbins is gradually reduced

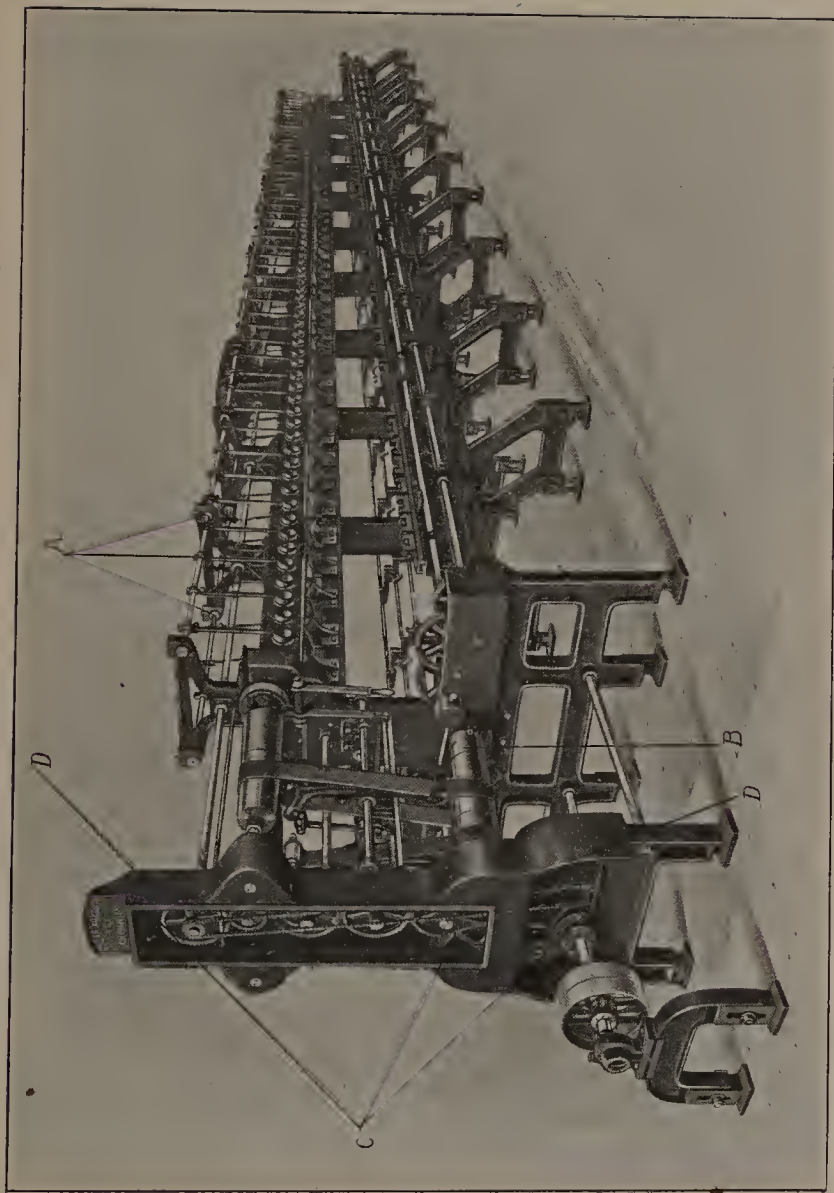


FIG. 29. DOUBLE-FRONTED BOBBIN SPINNING MACHINE WITH OSCILLATING
THREAD-GUIDE AND CONE DRIVE
(O. Kohorn & Co.)

in proportion to the thickness of the layer of thread which they contain. The mechanism for this purpose may be seen on the left-hand side of the above figure. It comprises two opposed conical belt pulleys, across which the driving belt is carried at a constant velocity by a fork which is carried forward by a shaft. The gearing *C* is housed in a casing *D*, which is closed and is filled with oil.

The above described bobbin spinning machines are usually provided with lacquered aluminium bobbins of a size not exceeding 12 to 15 cm. in length and 5 to 9 cm. in width ; but other machines are used in which the bobbins are usually constructed of glass, or occasionally of metal, and are of considerably greater dimensions, up to 25 cm. long and 15 to 20 cm. wide. When glass bobbins are used, it is obviously desirable to re-wind on to bobbins of considerably smaller dimensions before the twisting process, on account of the danger of breakage if roller twisting machines are used (Fig. 42). Large metallic bobbins cannot be used in this case, if only for the reason that at the high rate of rotation of the bobbins necessary for the twisting process (about 5000 revs. per min.), the centrifugal force would be too great in consequence of the large diameter, and the bobbins would easily be thrown off their supports, particularly if they were not quite symmetrical. In such cases, however, the so-called ring twisting frames can advantageously be used and are, in fact, frequently employed (see Fig. 43), in which the necessary rate of rotation for a reasonable output is not so high as in the so-called roller twisting machines ; in the former the rapid rotation is imparted to the spinning bobbin and not to the twisting bobbin as in the latter, and the twisting bobbin can be constructed of smaller diameter.

Centrifugal Spinning Machines (Pot Spinning Machines). The third variety of spinning machine is the so-called centrifugal spinning machine or pot-spinning machine. The advantages of the pot-spinning process are as follows : A special twisting process is unnecessary as the thread is twisted in the rapidly rotating spinning pot during the spinning process ; the capacity of the spinning pot is very large compared to that

of bobbins or reels, and, consequently, less time is wasted in interchanging the pots, and, moreover, less attention is required for the purpose of interchanging. The credit for the brilliant invention of this method of spinning artificial silk is permanently linked with the name of C. F. Topham.

The centrifugal spinning machine shown in Fig. 30 is constructed by the Düsseldorf-Ratinger Maschinen-und Apparatebau A.-G., Ratingen, and is provided with 60 spinning pots, 30 on each side of the machine. The machine is provided with an individual drive for each spinning pot, constructed either

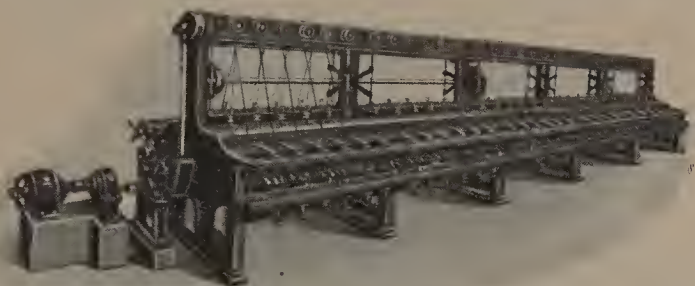


FIG. 30. DOUBLE-FRONTED CENTRIFUGAL SPINNING MACHINE
(Düsseldorf-Ratinger Maschinen-und Apparatebau A.-G.)

by Siemens-Schuckert or by Ramesohl & Schmidt, Olde, Westphalia.

A pot spinning machine constructed by the same firm with Siemens-Schuckert drive is shown in vertical elevation in Fig. 30A, whilst the Ramesohl & Schmidt drive is shown in Fig. 31. The frame of the machine, shown in Fig. 30, as in all textile machines, is constructed of light castings. The machine is divided into five sections, each containing six spinning pots, by a front partition, back partition, and four cross-partitions, which are interconnected by cross-stays. The main drive of the machine, including that of fans and spinning pots, is transmitted from the main shafting or from an electric motor of $4\frac{1}{2}$ to 5 h.p., coupled with its main shaft (Fig. 30).

In this case also, the gear-wheels are completely enclosed, and run in an oil bath. The adjustment of the various rates of withdrawal by the glass pulleys (Fig. 30A) is effected by the

displacement of a lever on the gear-wheel box in a similar manner to that employed in machine tools. The glass pulleys (galettes) are driven from a single shaft by finely toothed conical pulleys. The whole of the driving gear runs in an oil bath, which requires no attention. It is very important that

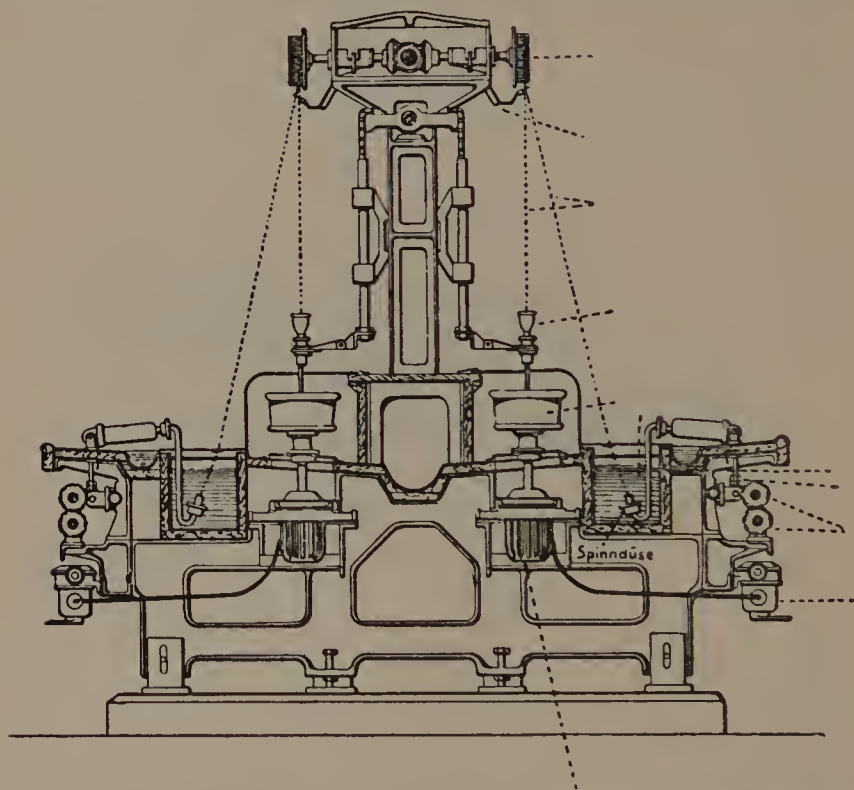


FIG. 30A. CROSS-SECTION THROUGH DOUBLE-FRONTED CENTRIFUGAL SPINNING MACHINE WITH SIEMENS-SCHUCKERT DRIVE
(Düsseldorf-Ratinger Maschinen-und Apparatebau A.-G.)

"Spinndüse" = spinning nozzle

the motion of the machine should be steady and free from vibration.

The spinning pots are situated in boxes lined with lead, which communicate with a ventilating flue contained within the machine.

The disposition of the spinning mechanism is shown in Fig. 30A, and in detail in Fig. 32. The spinning filter and also the connection for the spinning nozzles, are generally constructed

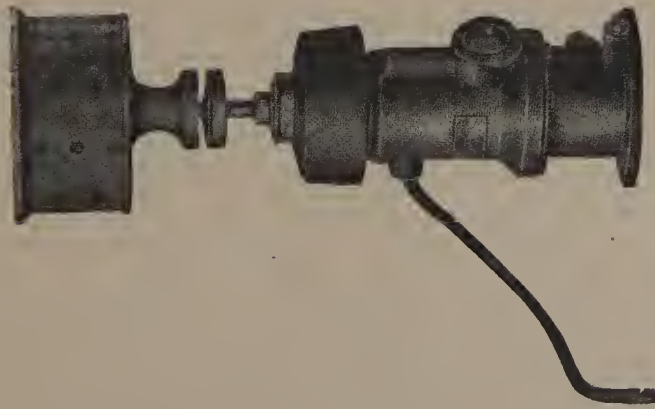


FIG. 31. RAMESOHL UND SCHMIDT
DRIVE FOR SPINNING POTS

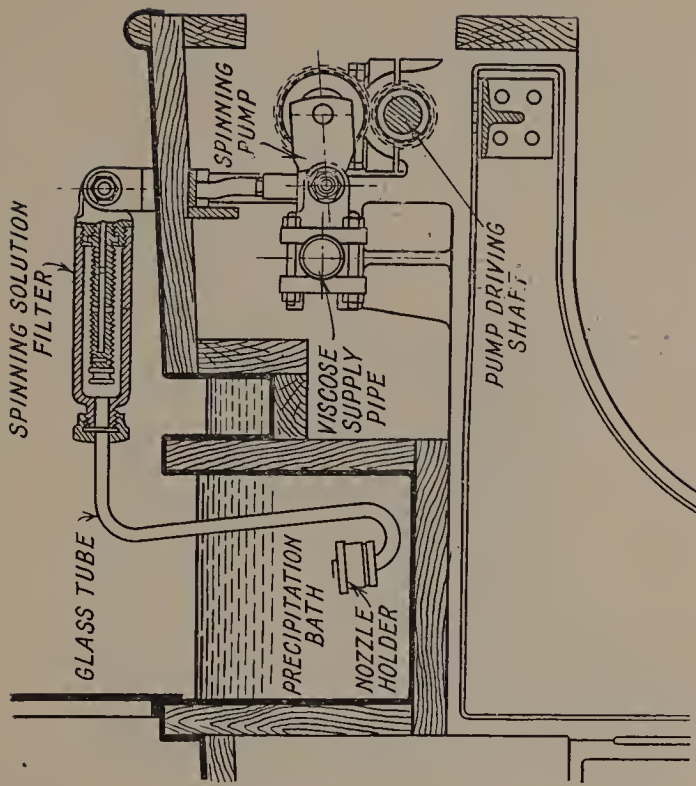


FIG. 32. SPINNING UNIT

of ebonite. The channels containing the precipitation bath are provided with overflow and discharge ducts. In order to enable the output of the pumps to be regulated in accordance with the various counts required, the machines are provided with an adjustable train of gear wheels housed in a gear-box. This gearing actuates the driving gear-wheel on the pump shaft shown in Figs. 30A and 32. The machine is naturally also

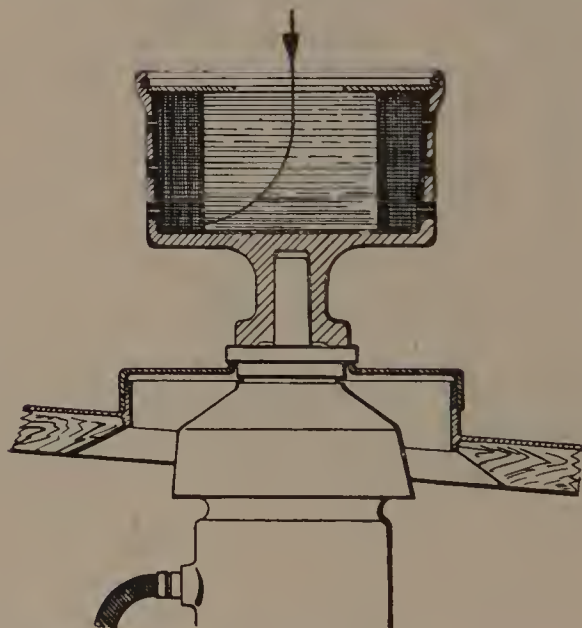


FIG. 33. SPINNING POT WITH CONICAL SEATING
CONTAINING FIBRE CAKE

adjustable with regard to rate of withdrawal and thread guidance, by interchanging the gear-wheels of the wheel train shown in front and to the left in Fig. 30.

Before the spinning motor is operated for the first time, the motor housing must be filled with oil through the oblique screw on the same (Fig. 31). On starting the motor the oil immediately circulates, and may be observed through the sight hole.

The spinning pots are affixed to the spindles by a seating, which was at one time cylindrical but which is now usually conical. Fig. 33 shows a spinning pot with a conical seating, and containing a cake of the spun material. The small spinning pot motors are driven by three-phase current, and the rate of

revolution is controlled by the periodicity of the current. As the current supply is usually of 50 periods, a second current circuit of correspondingly higher frequency has to be provided for higher rates of revolution. This transformation is effected by a frequency transformer. Such a machine consists of a

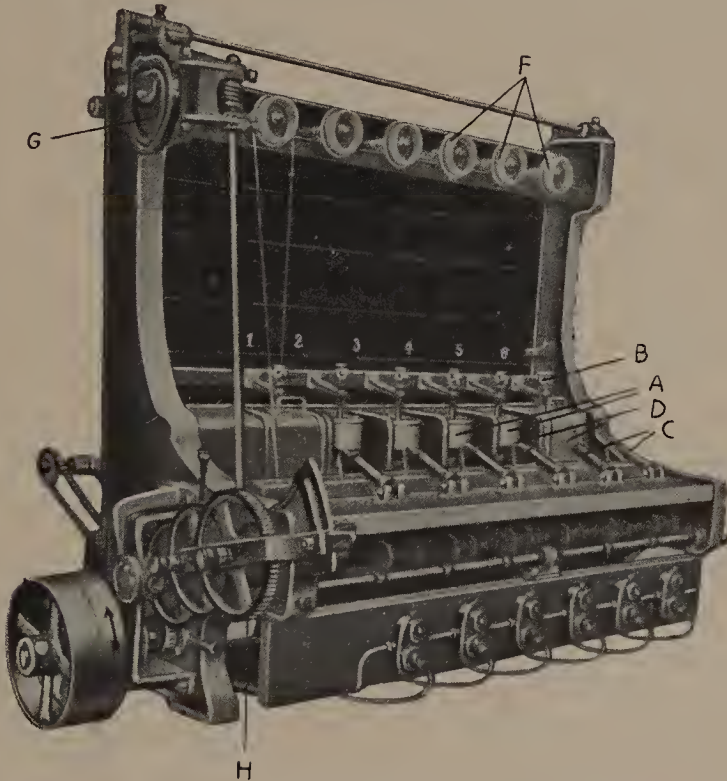


FIG. 34. LABORATORY CENTRIFUGAL SPINNING MACHINE
WITH 6 SPINDLES

(Düsseldorf-Ratinger Maschinen und Apparatebau A.-G.)

three-phase motor, which is driven in a three-phase current field by another motor. The normal three-phase current of 50 periods is supplied to the stator, and the secondary current is drawn from the commutator of the motor and used for driving the spinning pots. At 100 periods the rate of revolution without load and without a spinning pot is 6000 revs. per min., and with a spinning pot, 5600 revs. per min. The average voltage is then 135 volts, with radial coupling, and 78 volts with triangular coupling. The thread passes through the spinning

funnel (not shown in this figure but shown in Fig. 30A), and then downwards, as indicated by the arrow, into the spinning pot, where it adheres firmly to the wall of the pot under the influence of centrifugal force. In consequence of the up-and-down motion of the spinning funnel, the pot is continuously covered with a cake of thread through the whole of its height, corresponding to the distance of travel of the funnel. It is of the greatest importance for a uniform disposition of the thread that the funnel should be accurately centred. Fig. 34 shows a laboratory pot spinning machine with six pots, constructed by the Düsseldorf-Ratinger Maschinen-und Apparatebau A.-G., Ratingen, with individual drive by electric motors. The spinning pots *A* are to be seen in four compartments, whilst in two compartments they are closed by covers such as are usual during spinning, in order to avoid the introduction of spray from the spinning baths. These covers are usually constructed of aluminium, and are provided with an opening for the admission of the spinning funnel *B*. The filtering candles *C* are connected with the nozzle holders *D* by an ebonite screw-joint; the nozzle holders dip into the spinning bath. The thread pulleys, or galettes *F*, which have a separate drive, regulate the rate of withdrawal. A heart-shaped cam-disc *G* controls the oscillations of the spinning funnels. The rate of withdrawal and the thread guidance may be adjusted by interchanging gear wheels in the gear-box *H*, whilst the degree of twist of the thread—which is regulated by the rate of rotation of the spinning pots—can be adjusted by alterations of the rate of revolution of the individual electric motors driving the pots, which are not visible in the figure.

In addition to the above described centrifugal spinning process, which enables spinning and twisting to be carried out in one operation, the rotation of the spinning nozzle has also been proposed in order immediately to obtain a twisted thread. These proposals have been embodied in various patents, but no case of successful manufacture of artificial silk by this means has so far become known. If one considers that the thread as it issues from the spinning nozzle is still very soft and

only partially coagulated, it is comprehensible that an unsatisfactory composite silk thread is produced by twisting the fibres so produced, as their mutual adhesion cannot be avoided; moreover, the connection of the rotating nozzle with the supply pipe must be very perfect, a condition the realization of which is difficult, in view of the fact that the thread has to be rotated at 100 to 150 revs. per min., and is spun at a rate of 40 to 60 m. per min. (In the dry spinning process, the rate of withdrawal is four to six times as great as this.) This would entail a rotation of the spinning nozzle of at least 4000 revs. per min., which could hardly be achieved under the conditions of practical manufacture. Latterly, the textile industry has used untwisted or very lightly twisted threads to a small extent. Cuprammonium silk is particularly suitable for the production of such threads, as there is a natural tendency for the individual fibres to cohere without otherwise injuring the qualities of the thread.

Stretch Spinning Machinery. A special process, the so-called stretch spinning process, has been developed in connection with the wet spinning process, both on centrifugal and on bobbin machines. As has already been mentioned, all spinning processes are stretch spinning processes to a certain degree, as the rate of expulsion of the spinning solution from a nozzle is always less than the rate of withdrawal by the receiving mechanism. Such processes are not, however, described as stretch spinning processes in the ordinary sense, this term being reserved for processes in which the ordinary nozzle aperture of about 0.1 mm. diameter is replaced by nozzle apertures of 0.5 mm. diameter and over.

In order to obtain a fine fibre with such wide nozzle apertures, very considerable stretching must be produced. One advantage of this procedure is that obstruction of the nozzle apertures, which is always very troublesome in spite of the most careful filtration of the spinning solution, is avoided. Obviously, spinning solutions, in order to be suitable for this process, must coagulate very slowly and be capable of being drawn out to a fine thread during such coagulation. Very interesting publications regarding the stretch spinning process,

with illustrations, are due to H. Ost,* who investigated the process with a glass capillary of 0.20 mm. bore, and with cuprammonium cellulose solutions. In the figures on pages 106 to 109, we reproduce some of Ost's diagrams and photographs. (Figs. 35A, 35B, 35C, 36A, 36B, and 36C.)

Although Ost's drawings represent the process in somewhat exaggerated form, the photographs show how, with a uniform supply of spinning solution, the rate of withdrawal influences



FIG. 35A

Bath: NaOH solution at 59° C. Withdrawal: 6.5 m. per min. Pressure: 1000 mm. Hg. Capillary: 0.20 mm. bore, 3.5 mm. long.

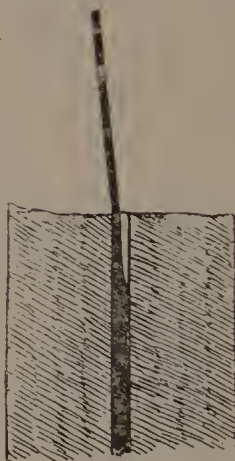


FIG. 35B

As 35A but at 49° C. and withdrawal 44 m. per min.



FIG. 35C

Bath: H₂SO₄ at 35° C. Pressure: 960 mm. Hg. Withdrawal: 74 m. per min. Capillary: 0.20 mm. bore, 3.2 mm. long.

the degree of stretch and, consequently, the fineness of the fibre. Photographs 37A, 37B, 37C, 38A, 38B, and 38C show the process when spinning viscose (37A, 37B, and 37C with a sulphuric acid-sodium sulphate bath, and 38A, 38B, and 38C with a pure sulphuric acid bath). Figs. (A) show the process without any pull, whilst in Figs. (B) the pull was about 30 to 40 m. per min. (the normal pull), and for (C), 85 to 90 m. per min.

In these cases, particularly in 38C and 38B, it will be observed that the fibre is reduced in thickness shortly after its liberation from the nozzle, and in 38C to some extent even within the nozzle aperture. In the acid sulphate spinning bath, however, the diameter of the thread remains unaltered after it leaves

* *Zts. f. angew. Chem.*, 31, 141 (1918).



FIG. 36A

Withdrawal : 9 m. per min.

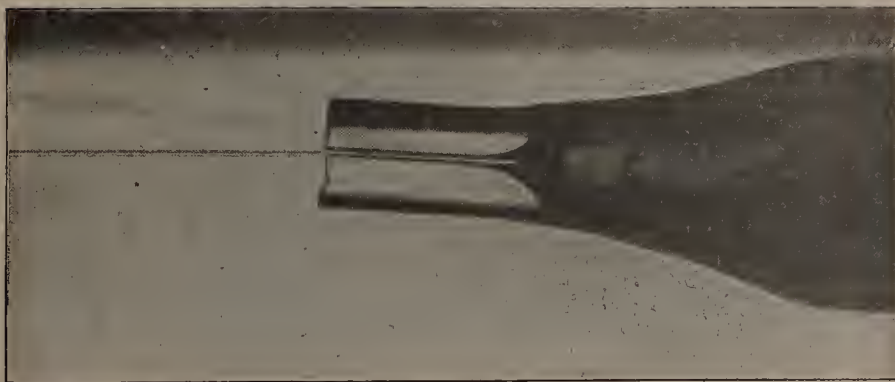


FIG. 36B

Withdrawal : 44 m. per min.



FIG. 36C

Withdrawal : 34 m. per min.
Bath : NaOH at 55° C.



FIG. 37A. ACID SULPHATE BATH



FIG. 37B. ACID SULPHATE BATH

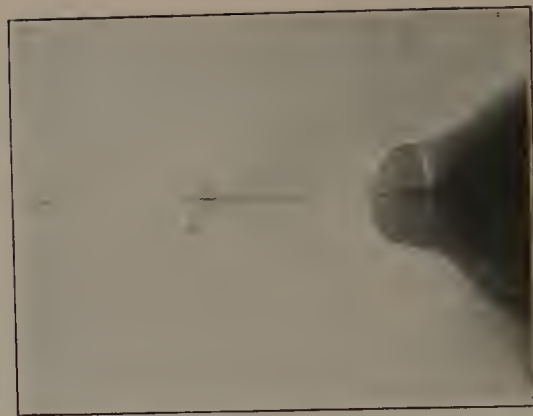


FIG. 37C. ACID SULPHATE BATH

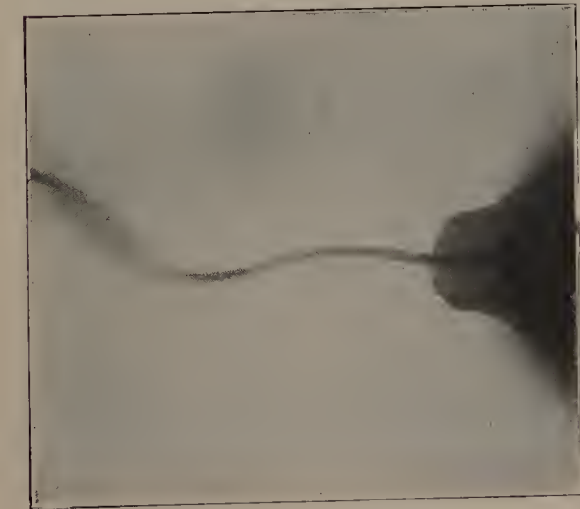


FIG. 38A. H_2SO_4 BATH

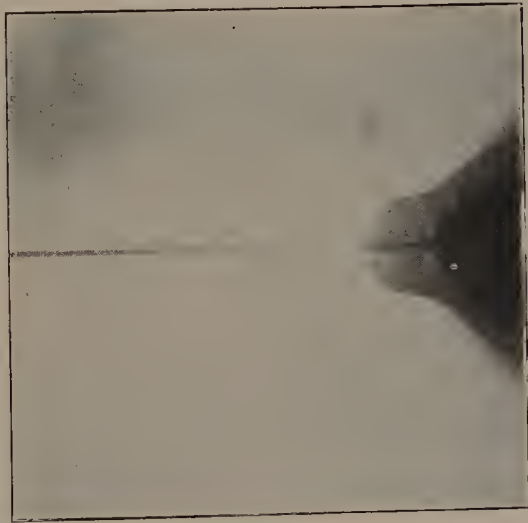


FIG. 38B. H_2SO_4 BATH



FIG. 38C. H_2SO_4 BATH

the nozzle aperture, possibly in consequence of the strongly osmotic action of this bath, as is described in German patent 187,947. The stretch spinning process is characterized by stretching and diminution of the fibre to about one-tenth to one-twentieth of the diameter which it possesses when extruded from the nozzle.

The stretch spinning process is at present probably exclusively used for the manufacture of cuprammonium silk of very

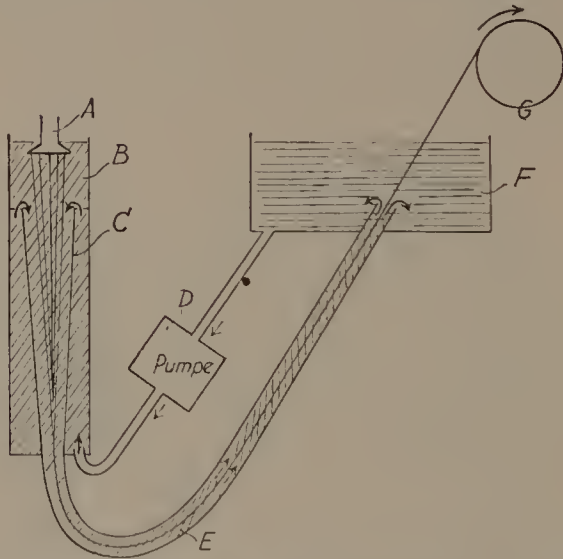


FIG. 39. DIAGRAM OF STRETCH-SPINNING UNIT

fine counts, in which it has achieved great success. The first patents, dealing with this process, are due to Thiele, its inventor, who died recently.

Fig. 39 is a diagrammatic representation of the apparatus used for the stretch spinning process. *A* is the multiple spinning nozzle from which the spinning solution issues into the precipitation bath in *B*. This bath flows into a funnel-shaped tube *C*, which decreases in diameter downwards and carries the thread with it. The spinning bath and thread are carried downwards in the direction of the arrows by the action of the pump *D*, which conveys the spinning bath liquid at a definite velocity. The rate of flow of the precipitating bath increases in accordance with the decreasing cross-section of the funnel,

so that the semi-coagulated thread is stretched in its passage through it. An upwardly bent tube *E* is attached to the lower end of the funnel and discharges into a vessel *F*, into which the precipitation bath and thread are impelled and the thread itself is wound on to the receiving mechanism *G*. The precipitation bath is recirculated by the pump and regenerated as may be necessary at some point in the circuit.

Proposals have been made to use liquids varying in character or in concentration at various points in this process, and this is possible by means of suitably modified apparatus.

The Spinning Room. In order to manufacture artificial silk with commercial success, the most important requirement, apart from quality, is the absolute uniformity of the product.* For this purpose the manufacture must be highly organized and considered in every detail before the erection of a works, so that the lay-out may be designed accordingly and that the utmost control and uniformity of production at all stages may be ensured.†

Accordingly, suitable lay-out of the spinning room of an artificial silk works is of very great importance, as light and air, easy control and accessibility, play a great part. The spinning room must form an organized link in the works processes. It must be closely adjacent to the department for the manufacture of the spinning solution and of the spinning bath, as unnecessarily long pipe lines are always a disadvantage. On the other hand, the departments for the after-treatment, washing (in the wet spinning process), twisting, and so forth, must adjoin the spinning room in accordance with the sequence of manufacturing operations; it is particularly important that the intercommunications should be short, convenient, and sufficiently broad, and that crossing of transport lines should be avoided. The room should more particularly be sufficiently high, in order to afford sufficient space for the ventilating hoods and mains, which are usually situated above the machines. The air supply mains and ducts for the pipe systems from

* See M. Duré, *Kunstseide*, 8, 505 (1927).

† See E. Wurtz, *Zts. d. Vereins Deutscher Ingenieure*, 58, 1581 (1925); *Chem. Apparatur*, 13, 13, 36 (1925); *Die Seide* (1927).

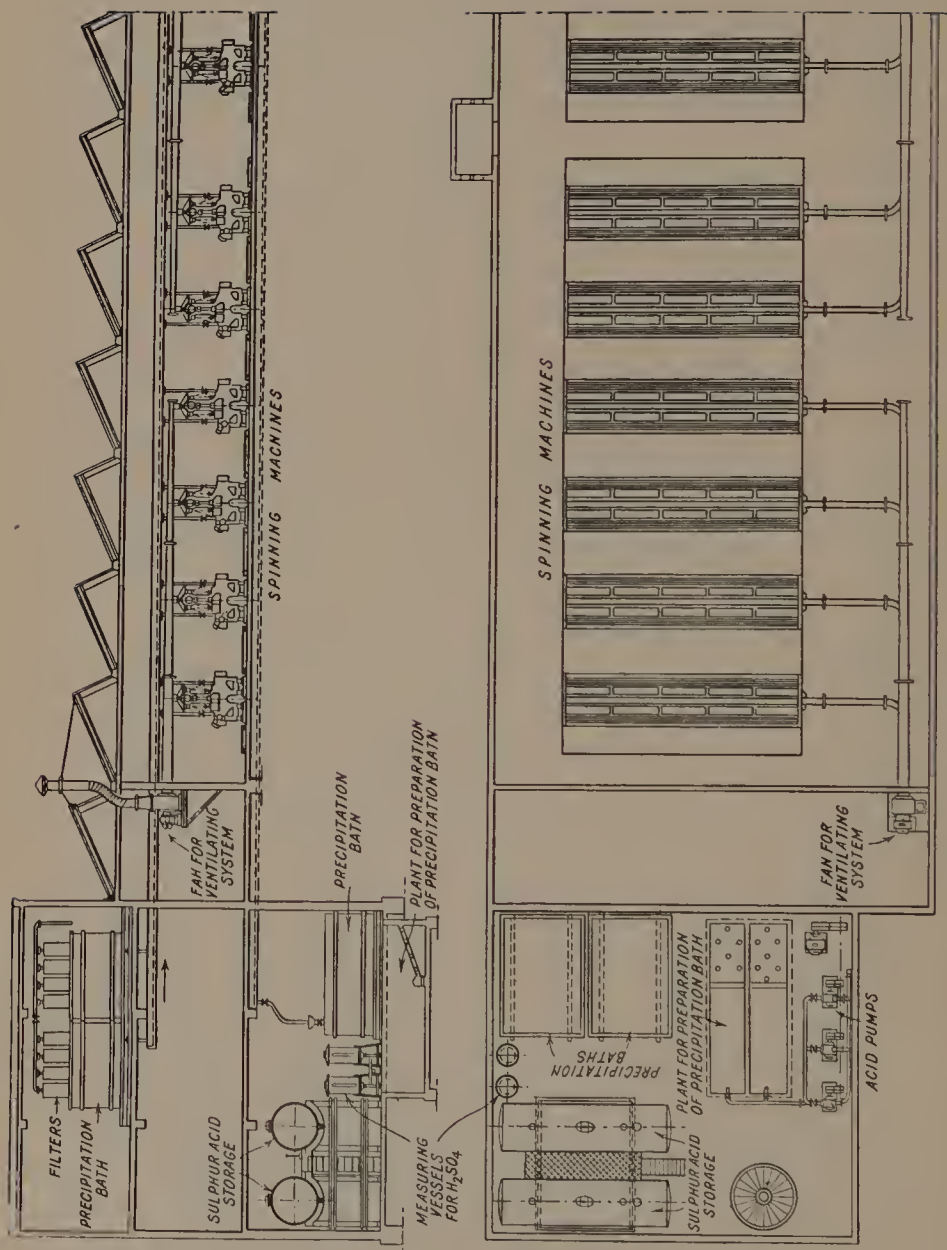


FIG. 40. SPINNING ROOM AND ACID ROOM

and to the spinning machines should be situated below the floor and be readily accessible. The arrangement of the containers for the precipitating baths and the facilities for preparing and regenerating these, should be organized in close association with the whole spinning system. It is convenient to prepare the precipitating bath in a room below the level of the spinning room. In this room, the sulphuric acid tanks and the measuring vessels should be placed, together with the tanks required for receiving the exhausted baths from the spinning machines which must be regenerated.

Fig. 40 shows diagrammatically the arrangement of the spinning room and of the acid room.

In practice, one may conveniently have several rows of spinning machines, leaving sufficiently wide gangways between them for conveying the raw material and removing the bobbins or spinning pots, so that the spinning room may have as nearly as possible a square floor space, by which means supervision is rendered easier and the distances through which materials and pipe lines have to be carried are made as short as possible. The precipitation bath, which is prepared and regenerated in the basement, is pumped by acid pumps through filters to the high level precipitation bath tanks. From these it flows down to the spinning machines under its own head, and is conveyed back into the containers in the basement. For the viscose process the containers for the precipitation bath are usually of wood, with a lead lining.

CHAPTER XI

APPARATUS FOR AFTER-TREATMENT AND FINISHING

Washing. The spun silk requires further treatment, which varies according to its method of production. In the wet spinning process it is especially important that the remaining traces of the spinning bath solution should be removed; in the cellulose nitrate process, the inflammable cellulose nitrate thread must be denitrated, whilst in the cuprammonium process it is necessary that the copper should be removed and recovered. Viscose silk is usually not only washed, but also desulphurized. These washings and chemical treatments are sometimes carried out after twisting and reeling, that is, after the actual textile treatment of the silk, but they may also be carried out on the spinning bobbin itself, that is, before the textile part of the manufacture, particularly in the bobbin-spinning process.

For this purpose, the spinning bobbins, which are usually of lacquered aluminium, must be perforated. The Belgian, A. Pinel,* first proposed an apparatus for this purpose. Fig. 41 shows diagrammatically Pinel's method of treatment. The bobbins 5, holding the silk, are superposed in columns of four, with suitable watertight washers between them. A large number of such superposed bobbins are then carried collectively on a movable frame into a vessel 1, in which the washing and other after-treatment is carried out. The liquid used for the after-treatment is circulated by the pump 11. The discharge pipe 12 is connected by distributing pipes 3 with the interior of the superposed bobbins, whilst the supply pipe 13 communicates with the interior of the containing vessel. The liquor is withdrawn through the pipe 12, and, consequently, flows from the container 1 through the layers of silk into the interior of the bobbins, by which means the whole of the silk is treated and the process can thus be completed with very great speed.

* French patent 547,834.

B. Borzykowski* introduced an improvement into this process by dispensing with the troublesome necessity for firmly uniting the rims of the bobbins by screw joints; for this purpose he uses conical seatings on the ends of the series of bobbins through which the inlet and outlet pipes are carried; these are constructed of soft, impervious material, and they therefore make a tight joint automatically under the action of the vacuum. A proposal has also been made to force the liquid by pressure from without, through the silk on the bobbins,† but probably

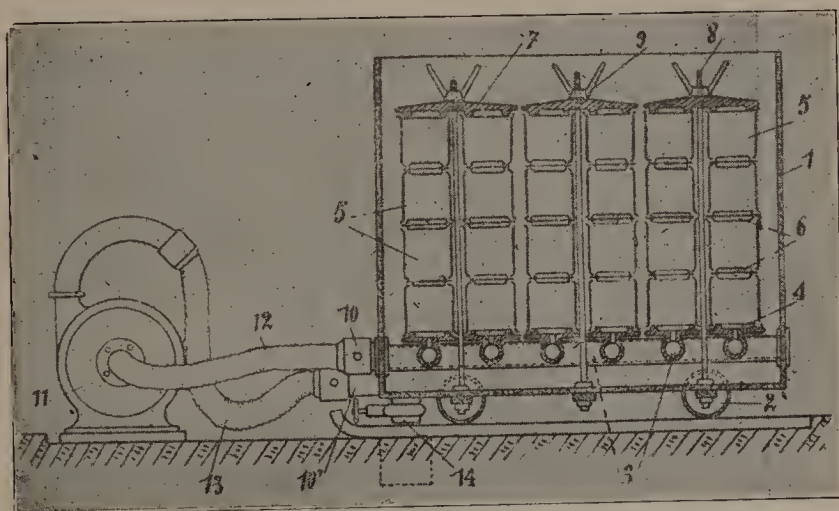


FIG. 41. PINEL'S WASHING APPARATUS

entails greater constructional difficulties than the use of a vacuum.

A large number of other proposals for this purpose are of earlier date. We may refer to the washing machine of Foltzer,‡ which washes by means of sprays in a manner to which the counter-current principle may be applied. This spray washing system also effects its purpose in a considerably shorter time than the method of working originally employed, in which the bobbins were inserted in large wooden vats filled with the washing liquid, which had to be renewed repeatedly at suitable intervals. It is not advisable to allow the washing liquid to

* Swiss patent 115,282/1924.

† Poizât, French patent 527,270.

‡ German patent 165,577.

flow through such vats, as otherwise the silk on the bobbins is easily washed away by the current and rendered worthless, at any rate with regard to its upper layers.

In order to wash hanks of staple fibre, Linnemann* proposes to dip them automatically for a short time in the washing or treating liquid, and then to raise them automatically, allow them to drain for a short time, dip them again, and so forth, until the treatment is complete; the hanks, which hang in frames, are then automatically conveyed to a position above a further tank filled with a suitable liquid, and so on, until the finished goods are finally removed and conveyed to the drying chamber.

Another hank washing machine is described by E. Wurtz.† A spray washing machine, which may be used either for hanks or for bobbins, has been designed by R. Linkmeyer,‡ and is sold by the Gesellschaft für Kunstseiden-Apparatebau, Bad Salzuflen, Lippe. In this machine the hanks are treated with the liquid in the form of extremely fine spray. The goods pass through all the baths on a special washing truck; in this machine a specially strong current of liquid is conveyed to the parts at which the goods are supported, so that the threads at these points, which are greatly compressed and in close contact, may be thoroughly treated, which is, of course, a matter of the greatest importance.

Although the most careful attention must be devoted to the continuous maintenance of a perfect spinning process, extremely careful washing and after-treatment is also of extreme importance, in order that the work may be properly carried out, as it is only possible in this way to attain a maximum yield of the best quality. Apart from the saving of wages, therefore, automatic machines which reliably effect washing and after-treatment processes are to be preferred to hand-labour.

Acetate silk alone, if it has been prepared by the dry spinning process, requires no further treatment apart from the complete removal of the solvent; this is undoubtedly a great advantage,

* German patent 377,346.

† *Die Seide*, 32, 232 (1927).

‡ *Leipzig. Mschr. f. Textilind.*, 42, 104 (1927).

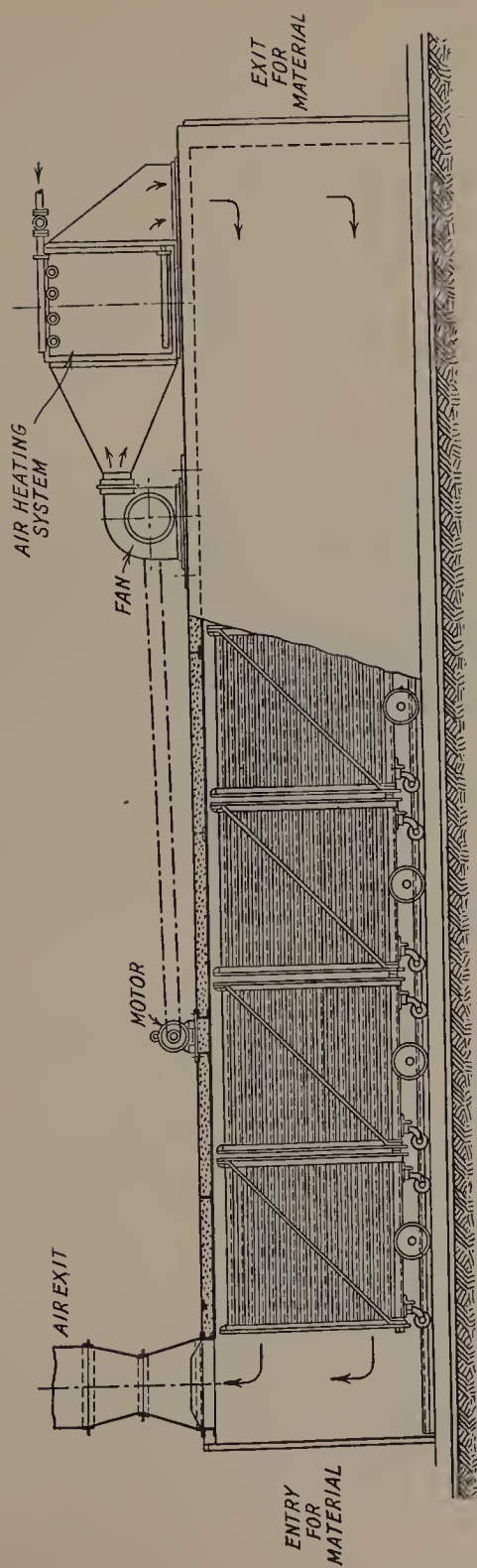


FIG. 42. DRYING PLANT
(Trocknungsanlagen—G.m.b.H., Berlin)

as such after-treatments always result in some deterioration of the quality of the silk.

Drying. In all spinning processes on bobbin spinning machines in which the wet spinning process is used, as described in the previous section, washing, and sometimes after-treatment, of the whole of the goods on the bobbins is a necessity. Before the actual textile treatment which follows, the goods must be dried, as artificial silk in a wet condition cannot withstand mechanical treatment or, at any rate, only

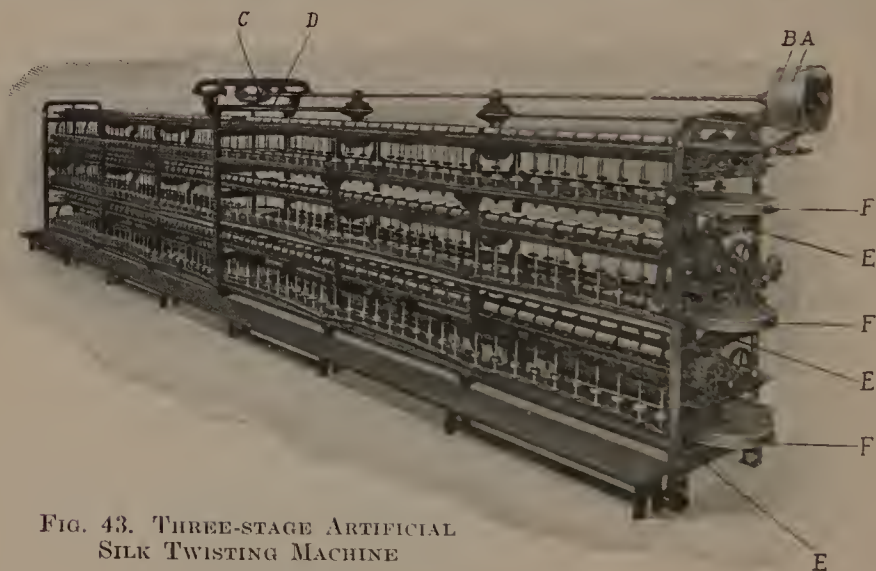


FIG. 43. THREE-STAGE ARTIFICIAL
SILK TWISTING MACHINE
(O. Kohorn & Co.)

if the greatest care is used, and, moreover, uneven shrinking would occur during such treatment through irregular drying of the goods.

In order to dry the silk, the spools are placed in rows of five or six on rods, which are usually placed horizontally in series on iron frames provided with wheels in superposed rows of about ten at a time. The frames, when so charged, are passed through a tunnel dryer as shown in Fig. 42, in which they are exposed to a counter-current of warm air.

The apparatus shown in Fig. 42 is supplied by the Trocknungsanlagen G.m.b.H., Berlin, W.9. We may also refer here to the very satisfactory drying apparatus of the firm of Haas, Lennep & Schilde, Hersfeld.

The action of such a tunnel dryer is obvious from the figure. The goods must first be thoroughly dried and are then brought to a definite degree of moisture content in an adjoining combined drying and re-conditioning apparatus, as when completely dry the silk is brittle and sometimes coheres to a certain extent, which may give rise to thread breakages and so-called lousy silk during the twisting process.

Twisting Machines. The washed silk, which may also have received an after-treatment on the bobbin, must now be twisted, unless it has been spun on centrifugal machines. For this purpose, twisting machines are used, such as the one shown in Fig. 43.

The machine shown is a double-sided, three-stage machine. It is driven from the middle of the machine by fast and loose pulleys *A* and *B*, but may be arranged with the drive at one end. The drive is transmitted by a spur wheel *C* to a vertical shaft *D*, which is provided with pulleys. These pulleys actuate the spindles by means of driving belts *E*.

The spindles are driven by the endless belts *E* which pass inside the spindle wharves and over three pulleys *F* at each end of the machine. Each belt is automatically maintained at the right tension by one of these pulleys.

The spindles are adjustable in order to ensure that they all rotate properly, and, moreover, adjustable guide pulleys are placed between the sets, but are not visible in the figure. The twisting spindles are supported loosely on strong U-frames. The spindles themselves are strong Rabbeth spindles, with an axis of the best steel provided with a lower belt. The spur wheels actuated by the vertical shaft *D* drive the middle row of cylinders, consisting of seamless brass tubing, by which the bobbins which receive the twisted yarn are turned by friction drive. The upper and lower series of cylinders are driven from the middle series by chains and chain wheels. These chains can be adjusted by special pulleys. According to the degree of twist the rate of withdrawal in the twisting machine is 20 to 30 metres per minute, whilst the speed of rotation for a twist of 150 turns per metre of silk is 3000 to 4000 revs. per min.

The machine is supplied by Oscar Kohorn & Co., Chemnitz.

Twisting machines with two stages only are much used. A twisting machine of very similar construction to that described above is the so-called "roller twisting machine," in which sheet iron rollers interposed between the rows of spindles and parallel to the same are actuated by the drive, whilst the spindles themselves are turned by spindle belts driven by these rollers. In this case a special belt is obviously required for each spindle, and if any of these have to be replaced, the machine must be stopped for the purpose. Both these forms of machine have their special advantages and disadvantages and require careful supervision and observation in order that the twisted artificial silk may acquire as uniform a twist as possible. In spite of this, however, variations in the degree of twist of about 20 per cent are not uncommon.

We must also mention here the ring twisting frames, already referred to, which are especially common in the highly developed Swiss artificial silk industry. Whilst in the above-mentioned machines the spinning bobbin, from which the thread is withdrawn, revolves at a high speed in order to produce the twist, and the twisted thread is received at a definite rate by the receiving bobbin, which revolves at a correspondingly low speed, in ring twisting frames the receiving bobbins, which revolve very rapidly, are of small diameter and considerable length, whilst the twisted thread is withdrawn slowly from the spinning bobbin. These machines are called ring frames on account of the small ring adjusted to the weight of the thread, through which this runs, exactly as in the flyer machine of textile spinning mills.

The ring twisting frames operate on a principle exactly opposite to that of the stage or roller twisting machines. In these latter, the spinning bobbin, which holds the thread which is to be twisted, is placed on a rapidly revolving spindle, and the thread which is twisted by the revolutions of the spindle is withdrawn and wound on to a horizontal receiving bobbin, which is driven by an adjustable revolving cylinder. The thread is conveyed to the receiving bobbin by an oscillating thread guide.

In the ring twisting frame (Fig. 44), the spinning bobbins *B* are placed on pins *A*, and the artificial silk is withdrawn by the

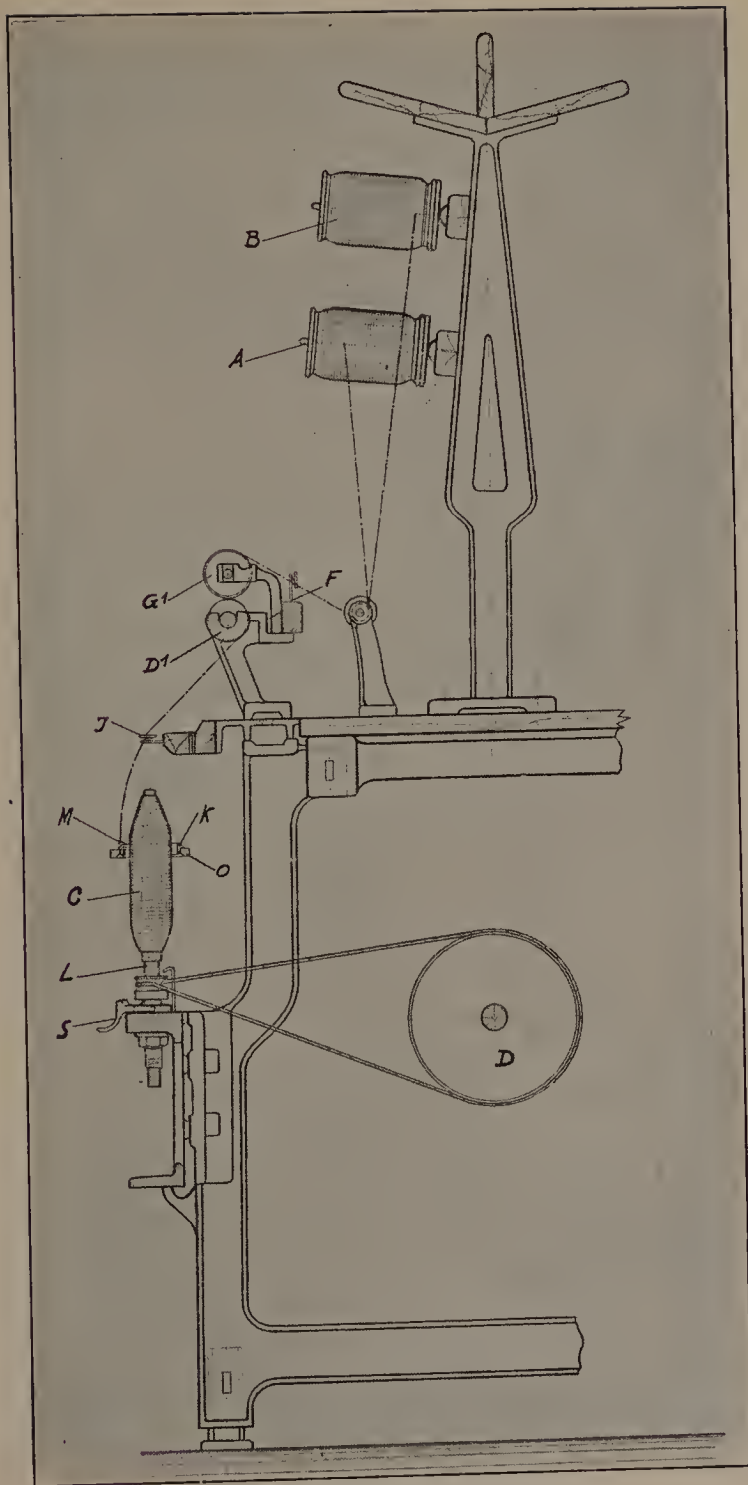


FIG. 44. RING TWISTING FRAME
(C. Hamel A.-G.)

roller-train G , which may comprise a lower roller D_1 of iron, or iron coated with brass, with which a pressure roller G_1 , covered with soft rubber, engages, in order to ensure a steady withdrawal of the smooth thread. The thread withdrawn by these rollers now passes through the lappet loop J above the spindle L , and through the ring travellers M on the ring K to the spindle L , which supports a cardboard or wooden spool C , on which the thread is wound. The ring rail O ensures the pirn form of the yarn cake by a combined oscillatory movement and continuous upward travel.

The twist is imparted by means of the rapidly revolving spindle L combined with the ring traveller K , revolving round the stationary ring O in such a manner that the traveller equalizes the difference between the rate of withdrawal by the rollers G_1 and D_1 and the rate of winding of the spindle L , which is effected by the fact that the tangent of the course of the thread from the ring traveller K to the yarn cake C which is being formed, is constantly altered.

The power requirements of the ring twisting frame vary with the rate of revolution of the spindle and the width of the ring, or the ring weight, which is used. One may reckon on the average that 40 to 50 spindles require 1 h.p.

The amount of labour required by these machines depends on the twist which is imparted to the thread. It is found that with 100 twists per metre one girl can serve about 100 spindles, and with a twist of 200 per metre, one girl can attend to 180 to 200 spindles. The spindles are about 83 mm. apart. A ring twisting frame with 200 spindles requires about 4 h.p.

As in all places in which textile goods are treated, a certain degree of humidity of the air, which may not be reduced, must be present in the twisting room. Apparatus for this purpose is supplied, for example, by Dannenberg & Quandt, Berlin-Lichtenberg. L. Kirberger,* and others have dealt with the question of the automatic regulation of the degree of humidity of the air.

After twisting, the goods are usually moistened or steamed on the bobbins in order to stabilize the twist.

* *Kunstseide*, 9, 142 (1927).

Reeling Machines. After twisting, the material is reeled. For this purpose, machines are used of the character shown in Fig. 45. This machine is supplied by Carl Hamel A.-G., Schönau, near Chemnitz.

Each reel is designed to receive ten hanks, so that ten twisting bobbins can be dealt with simultaneously. The machine is so arranged that if a thread breaks the reels stop automatically, in consequence of the fall of the movable thread guide. The rate of withdrawal during this operation may be fairly high,

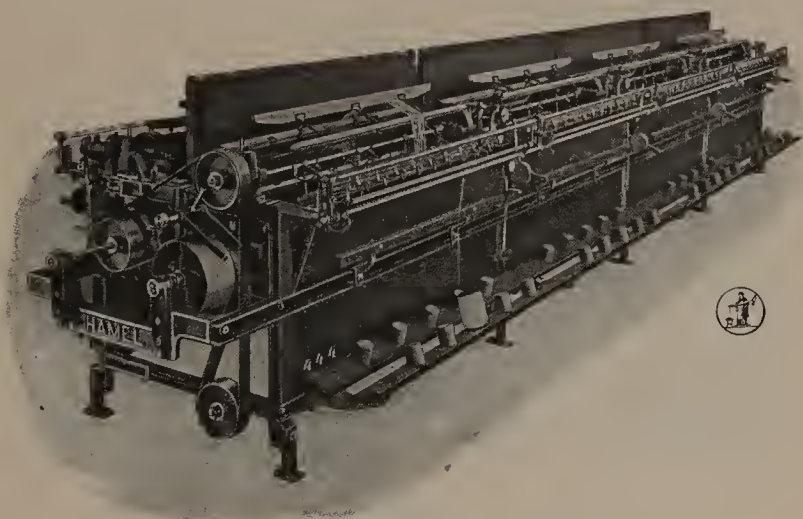


FIG. 45. REELING MACHINE
(C. Hamel A.-G.)

up to 250 metres per minute and more. The power requirements for 8 such reels are about 1 h.p. The output of such a machine depends on the skill of the operative, and in general one reeling machine with 10 spindles may be assumed to deal with 40 spindles of the stage twisting machine at a normal twist of 120 to 140 per metre. One or two ribs of the reeling frame are collapsible, so that the hanks may easily be removed from the rim of the frame. Satisfactory cross-winding of the thread on the reel, as shown in Fig. 46, is obtained by a reciprocating thread guide. This cross-winding is of the greatest importance for the quality of the silk, more particularly in order to enable it to be readily unwound subsequently.

The hanks contain 1800 to 3600 m. of thread, and the

reels are provided with revolution counters and stop automatically when the required amount has been wound ; after winding the hanks are removed and passed to the skeiner, who provides them with skeining threads. Each hank is provided with three or four skeining threads, and the two ends of the thread are firmly knotted to one of these. In this way, means are provided to enable the hank to be easily unwound after further treatment, such as dyeing. Special attention has to be paid to this point.

Reeling Pot-spun Artificial Silk. In the pot-spinning process, twisting is carried out simultaneously, so that the thread

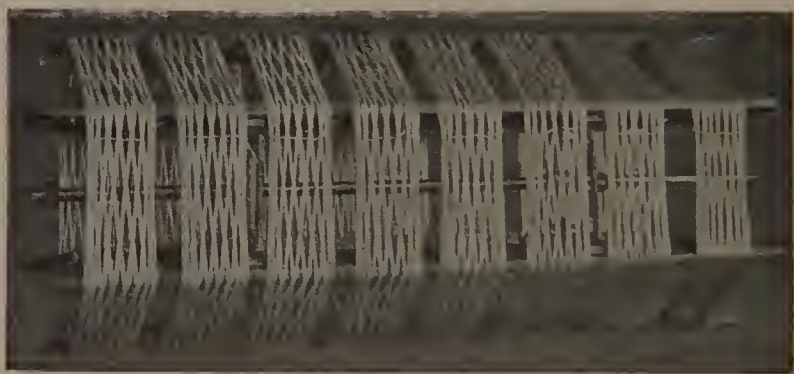


FIG. 46. REEL CARRYING STRONGLY CROSS WOUND ARTIFICIAL SILK. BEFORE SKEINING

produced by this method can immediately be wound on to reels. This subsequent operation must, however, be carried out directly with the spinning cake removed from the spinning pot, by reversing it before the thread is submitted to further treatment ; that is, the cakes must be wound on to hanks, if necessary, whilst still moistened with acid. In order to avoid this undesirable necessity, various proposals have recently been made. For the purpose, reeling machines are often used such as those supplied by Oskar Kohorn & Co., Chemnitz, and shown in Fig. 47. As such winding machines are operated by women, they have to stand idle at night, and it is therefore necessary to provide that the pot-spinning cakes produced during the night shift are so stored that it is impossible for the silk, moistened with acid, to dry. Attempts have

recently been made to wash these spinning cakes free from acid before winding, which would certainly be very desirable.

Chemical After-treatment. The after-treatment of the silk, in so far as it has not already been performed immediately after spinning, is now carried out on the finished hanks. The hanks are turned by workmen in the after-treatment baths, in simple wooden vats, in exactly the same way as is usual

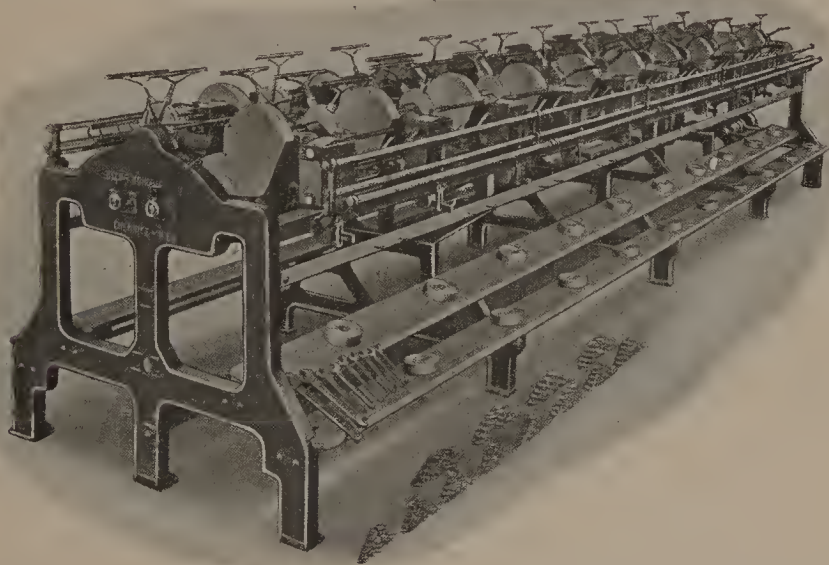


FIG. 47. REELING MACHINE FOR MOIST, ACID ARTIFICIAL SILK FROM SPINNING POTS, WITH INDIVIDUALLY ACTUATED, REMOVABLE REELS
(O. Kohorn & Co.)

for dyeing. Special attention must be paid to very careful treatment of the silk hanks, in order that the quality of the silk, and more particularly the capacity for being wound, may not be impaired.

Apparatus may be used for the purpose similar, for example, to Linnemann's washing machine for staple fibre already described on page 116, or a spray apparatus may also be used. (See pages 115 and 116.)

After this after-treatment, the silk is washed, soaped, hydro-extracted in centrifuges, and dried in drying ovens in a manner similar to the drying of wood pulp and the intermediate drying of silk already described. For this purpose it

is conveyed into the drying ovens on movable frames and dried at about 60° C. Silk produced by the centrifugal process is dried in similar drying ovens, but the silk hanks are placed in so-called tension frames, which are so arranged that the goods are submitted to considerable tension during drying. This tension has already been produced in the silk spun on bobbins during the intermediate drying ; its purpose is more particularly to endow the silk with a greater lustre than is possible if it is not applied.

After drying, the silk is sorted into various qualities. In order that an artificial silk works may be remunerative, it is particularly important to carry out the operations in such a manner, that as much first quality silk is produced as possible. This result may be obtained by careful attention to the chemistry of the process and also by extreme care in the handling of the silk at all stages ; the quality is of additional importance, as uniform dyeing properties are conditional on good quality. The silk is finally packed in parcels of about 5 kg., and is then ready for marketing.

CHAPTER XII

THE CELLULOSE NITRATE PROCESS

Production of the Spinning Solution. The method of preparing the spinning solution for cellulose nitrate silk depends on whether the dry or the wet spinning process is to be used. Formerly, cotton or linters were used for both processes. Linters are obtained from the waste fibres which remain on the seed after the long cotton fibres have been removed. Chemically, they consist of the same material as the more valuable cotton.

Before nitration, the raw material undergoes a process of purification which removes the fat and all other impurities. In consequence of the experience gained during the war, it is now possible to use sulphite pulp in the form of tissue paper for the nitration, and this material is now almost exclusively used for the purpose in Europe. Great attention must, however, be paid to absolute uniformity of the supply, as otherwise the varying degrees of viscosity obtained when using these materials make artificial silk manufacture impossible.

For the dry spinning process used by Chardonnet, a nitration acid was used containing 19 to 19.5 per cent of water, about 17 per cent of nitric acid, and 63.6 to 64 per cent of sulphuric acid; whilst for Lehner's wet spinning process, according to Guttman,* a nitration acid is used containing 15 per cent of water, 37.5 per cent of nitric acid, and about 48 per cent of sulphuric acid. The duration of the nitration is 1 to 1½ hours, and the temperature 40° C. The higher the nitration temperature, the lower, in general, is the viscosity of the dissolved cellulose nitrate solution. According to Becker,† a suitable nitration acid for artificial silk has the following composition: 14.7 per cent of water, 31.5 per cent of nitric acid and 53.8 per cent of sulphuric acid. According to his account, the duration of the nitration is 10 minutes only at 50° C.

* Guttman, *Schiess-und Sprengmittel* (1900), p. 101.

† F. Becker, *Die Kunstseide* (Halle, 1912, W. Knapp).

Lunge* has carried out a detailed investigation of the percentages of nitrogen obtained with mixed acid of various concentrations.

In general, a cellulose nitrate of the highest degree of solubility is obtained with a nitration acid containing 19 to 19.5 per cent of water. For reasons of economy, as low a percentage of nitrogen as possible in both the nitrated product and in the nitration acid is desirable. The determination of the nitrogen is carried out according to the method of Schulze-Tiemann† by reduction with ferrous salts, or with the nitrometer.

According to Hans Ambromn‡ the nitrogen may also be determined by observation with the polarization microscope. This method is much used in nitration works and gives very reliable results when carried out by experienced specialists.

The proportion of material nitrated to the weight of nitration acid is usually 1 : 30. After nitration is completed, the excess of nitration acid is drained off and the material is treated in aluminium centrifuges. The cellulose nitrate is then washed free from nitration acid, first in cold and finally in hot water. It is then disintegrated in a pulp engine. This disintegration of the nitrated fibre is absolutely necessary in order to stabilize it. The pulped cellulose nitrate is then treated with water at 100° C., which temperature is obtained by introducing direct steam, and is then once more centrifuged. It is now ready for use, and contains about 30 per cent of water, which may be removed in so-called displacement vessels. These are cylindrical vessels, into which the cellulose nitrate is compressed by an air-driven piston to about 12 atm. pressure, after which alcohol is forced into the mass from below and completely replaces the water.

According to other processes, a spinning solution is used consisting of a solution in ether-alcohol of cellulose nitrate which contains water amounting to as much as 25 per cent. Solutions containing water are in no case suitable for the dry spinning process.

* Lunge and Bebie, *Zts. f. angew. Chem.*, 14, 483 (1901); Lunge and Weintraut, *Zts. f. angew. Chem.*, 13, 393, 441, 467 (1899).

† Lunge-Berl, *Chemisch-techn. Untersuchungsmethoden*.

‡ Dissertation (Jena, 1914).

For the dry spinning process, cellulose nitrate solutions in ether-alcohol are used, containing 20 to 25 per cent of cellulose nitrate. For the wet spinning process, concentrations of cellulose nitrate greater than 15 per cent are not used. All danger of evaporation is avoided when dissolving the cellulose nitrate in mixtures of ether and alcohol by using large closed tinned or bronzed vessels. The collodium solution, as the spinning solution is called, must not come into contact with iron, and all pipes and apparatus must be constructed of bronze or glass.

After solution, the spinning liquid must be carefully filtered, which operation is carried out in filter presses, with the use of compressed air. The concentrated dry-spinning solution requires an air pressure of 70 atm. for this purpose, and for that reason very strongly built apparatus must be used for this process. After filtering, the spinning solution is allowed to stand for a time, more particularly in order to allow the air bubbles which it contains to rise to the surface, as should these enter the spinning nozzle they would cause the thread to break, or at least give rise to a weak spot.

Denitration. After the spinning solution has been spun in the usual manner and the threads then twisted and reeled, they still consist of exceedingly inflammable cellulose nitrate, and must, therefore, be denitrated prior to further operations. Denitration is carried out by means of solutions of alkali hydrosulphides; for example, 5 per cent solutions of sodium hydrosulphide are used. The temperature during denitration is maintained at about 40° C. Ammonium hydrosulphide is not so suitable for denitration, as it weakens the fibre. In his works, Count Chardonnet formerly used a 3 per cent solution of calcium hydrosulphide at about 45° C.

The loss of weight during denitration is quite considerable, in consequence of the removal of the nitrate groups, and may amount to as much as 30 per cent, varying with the percentage of nitrogen of the original cellulose nitrate. Denitration is accompanied by a very considerable loss of strength, particularly in the wet condition. Denitration must be carried out in a very uniform manner, as uneven denitration results in very uneven absorption of dyestuff when the material is

ultimately dyed. If the denitration is carried too far or takes place too violently—which is indicated immediately by a rise in the bath temperature—degradation of the cellulose hydrate and a loosening of the fibre structure is caused, and results in a considerable and disadvantageous reduction in the fibre strength. The time required for denitration is about 2 hours. The process is carried out in the usual manner in vats, and the hanks are handled in a manner similar to that usual in hank dyeing, or machines can be used for the purpose. The machines of Linnemann already described on page 116 may be used, or spray washing machines, which are very commonly used, or the new Gerber washing machine, supplied by I. P. Bemberg, in which the hanks are suspended from porcelain rollers which slowly revolve, first in one direction and then in the other, above the surface of the bath.

After denitration, the silk consists essentially of so-called cellulose hydrate ; apart from the character of its cross-section already referred to, cellulose nitrate silk can always be rapidly and easily distinguished from other artificial silks by the blue coloration obtained with diphenylamine and sulphuric acid, as the denitrated silk still contains about 0.1 per cent of nitrogen.

After denitration, the hanks are washed, soaped, sometimes bleached, and dried and sorted in the usual manner.

CHAPTER XIII

CELLULOSE ACETATE AND CELLULOSE ETHER PROCESSES

THE inflammability of the cellulose nitrate thread, otherwise characterized by its extremely stable character and great resistance to water, led to a search for other cellulose esters which would not share with nitric acid esters the undesirable property of being explosive. Schützenberger first produced a cellulose acetate in 1865, and very much work has been carried out on this substance since that date. Very much information on the cellulose acetate compounds obtained by acetylation is contained in the comprehensive work of Ost.* We may also refer to the work of W. Weltzien† and to that of K. Hess, already mentioned. Ost shows how a uniform cellulose triacetate may be produced by avoiding temperature rise and by using zinc chloride as a catalyst, in a mixture of acetic anhydride and glacial acetic acid. This cellulose triacetate dissolves in chloroform, tetrachlorethane, glacial acetic acid, pyridine, and other solvents, and more particularly in chlorinated aliphatic liquids. Industrially, however, "secondary" cellulose acetate (cellite) is employed, soluble in acetone, which is only produced by a special hydration treatment of the triacetate by dilute mineral acids, or strong organic acids, as described by Eichengrün, Becker and Guntrum,‡ and by Miles.§ Both this special treatment and the actual acetylation must be carried out with care, as otherwise the cellulose complex is too strongly degraded, with consequent reduction of the viscosity. H. Pringsheim recently|| showed that by heating a cellulose triacetate to definite temperatures, perfectly definite reductions of the viscosity of the original material are obtained, quite

* H. Ost, *Zts. f. angew. Chem.*, 19, 999 (1906), and 32, 66 (1919).

† *Liebig's Ann.*, 425 (1923).

‡ German patent 252,706/1905.

§ U.S. patent 838,350/1906.

|| Lecture at the General Meeting of the Verein der Zellstoffchemiker und Ingenieure, Berlin, 3rd December, 1927.

independently of the duration of heating. The various qualities of cellulose acetate silk produced commercially possess very varying degrees of viscosity, in spite of almost equal contents of acetyl groups (53 to 54 per cent calculated as acetic acid), as can easily be shown by dissolving them in acetone. The silk which has the greatest strength also shows the highest viscosity. A limit to the latter is only necessitated by the difficulty in filtration and removal of air bubbles.

As a raw material, cotton, or the best quality of wood pulp is used, which may previously be subjected to mercerization or other treatment in order to increase its reactivity. The so-called "primary" cellulose acetate solution is the solution containing the reaction product, together with all additions to the acetylation mixture, glacial acetic acid being the solvent in this case. If glacial acetic acid is replaced by benzene in the acetylation process, the resulting cellulose acetate is not dissolved. The cellulose acetate may be precipitated from the primary cellulose acetate solution by pouring into water, and can then be washed and dissolved in acetone after a special after-treatment. Miles* carries out the after-treatment directly in the solution of the primary acetate, and then precipitates the product. A practical method of operation is, for example, the following—

1 kg. of acetic anhydride and 1 kg. of glacial acetic acid are mixed with 15 gm. of concentrated sulphuric acid of sp. gr. 1.84; 250 gm. of cellulose are introduced into this mixture with constant stirring and simultaneous cooling. The temperature must not rise about 30° C. After 4 to 5 hours, the cellulose is completely dissolved and the reaction is finished. The triacetate which is produced is separated by pouring the acetylation mixture into a large excess of water. The acetate which is so precipitated is well washed, dehydrated in a centrifuge, and dried. Instead of sulphuric acid, zinc chloride, for example, can be used as a catalyst and has a somewhat milder action, so that the course of the reaction is retarded.

The patent literature describes a large number of processes of converting the triacetate as produced by the above process

* U.S. patent 838,350/1906.

into an acetone-soluble form. These processes all depend essentially on a weak, partial saponification of the primary acetate, with simultaneous depolymerization of the cellulose micella,* by the use of either weak acids, or acid salts or bases. Apart from acetone, mixtures of liquids which will not individually dissolve cellulose acetate can be used as solvents, such, for example, as mixtures of alcohol with benzene, dichloroethylene, formic acid esters and ethers. Such mixtures are analogous to the mixture of alcohol and ether, which dissolves cellulose nitrate. Tetrachlorethane is also a good solvent for cellulose acetate, but is very poisonous.

Before being dissolved to form a spinning solution, the secondary acetate must be washed until completely free from acid. Acids, more particularly sulphuric acid, which is used as a catalyst during acetylation, are very obstinately retained. V. Hottenroth† has described a very simple and practical method of determination of this acid. He dissolves the acetate in concentrated hydrochloric acid, which decomposes it, and hydrolyses the cellulose so that the solution may be diluted with water and the sulphuric acid determined with barium chloride.

Owing to its property of being soluble in more or less easily volatile organic solvents, cellulose acetate silk, in common with cellulose nitrate silk, may be produced both by the dry and by the wet spinning processes. Processes are also known in which two immiscible liquids of different chemical character and different specific gravity are superposed and used as a precipitating bath. In such processes the heavier liquid, which acts first, is intended to act as a slow precipitant of a material which can be drawn out to very thin fibres, whilst the second, lighter liquid effects further coagulation. For the dry spinning process, which is usually employed, solutions containing about 20 per cent of cellulose acetate are used.

The cellulose acetate process has the advantage over all other artificial silk processes that, more particularly when dry spinning, the spun silk has merely to be twisted and reeled and

* H. Ost, *Zts. f. angew. Chem.*, 33, 79 (1919); Knoevenagel, *Zellulosechemie*, 3, 113 (1923).

† V. Hottenroth, *Chem. Ztg.*, 38, 515 (1914).

is then finished. This simplification is a very advantageous feature of the process, as all after-treatments deteriorate the quality of the product. Another very great advantage of the process is the high rate of withdrawal which can be used, just as in the cellulose nitrate dry spinning process. This amounts, for example, to 4 to 6 times the rate of withdrawal when spinning viscose silk.

The silky appearance of acetate silk is very attractive. The strength of acetate silk, especially in the wet condition, of which one hears so much, is by no means very exceptional, as may be seen from the table on page 52, more particularly if one considers the absolute strength, which is the quality of practical importance.

The advantages of acetate silk are to some extent counter-balanced by the great difficulties of producing a cellulose acetate capable of yielding a thread of uniform quality. The addition of softening agents has been proposed in order to increase the elasticity, such as triacetin, tricresyl phosphate, triphenyl phosphate, toluene-sulphamide, and other substances.*

Another disadvantage of the process is the high price of acetic anhydride, which cannot be used in the theoretical quantity, as it must, in addition, be present in sufficient quantity to combine with the water of reaction to form acetic acid.

In acetate silk processes, as in others, it is of fundamental importance that the solvents should be recovered as completely as possible. In practice about 90 per cent of these are recovered.

A disadvantage of acetate silk is constituted by its great sensitiveness to heat, which, for example, renders it practically impossible to iron fabrics containing it.

Acetate silk cannot be dyed by the ordinary dyeing processes. It is, therefore, much used for so-called fancy threads, in materials in which it remains colourless during dyeing, and thus produces a white pattern. Special classes of dyestuffs had to be invented for acetate silk in order to overcome the difficulties in dyeing that material.

* See J. Scheiber, *Lacke und ihre Rohstoffe* (J. A. Barth, Leipzig, 1926) p. 337.

According to Kurt Hans Meyer,* dyeing with these substances consists in solution of the dyestuff in the cellulose acetate gel. Naturally, such dyestuffs can be removed completely from the fibre by washing, as they are not combined with it.

We have already shown cross-sections of acetate silk, which resemble those of cellulose nitrate silk, owing to the similarity in the method of production of the two materials.

We refer the reader to numerous patents dealing with acetate silk and cellulose acetate by Farbwerke vorm. Bayer & Co., Leverkusen, by Dreyfus, Henckel von Donnersmarck, Lederer and Eichengrün.†

On burning individual fibres of acetate silk, small black spherules are produced at the burnt ends of the threads, similar to those produced with unweighted natural silk. It can, however, readily be distinguished from the latter by the difference in the odour when burning, also by its solubility in organic solvents in so far as it has not been saponified,‡ and also by the shape of its cross-section.

Acetate silk is extremely easily saponified, and is then converted into a cellulose hydrate thread of much lower strength, similarly to the alteration of cellulose nitrate on denitration.

On the properties of modern acetate silk, see also R. O. Herzog.§

The importance of cellulose acetate in the varnish industry steadily increased during and since the War, more particularly for aeroplane dopes, on account of its non-inflammability. For the same reason, the importance of cellulose acetate films is steadily increasing.

THE CELLULOSE-ETHER PROCESS

One cannot at present speak of an actual working process for the manufacture of artificial silk from cellulose ethers, as

* Kurt Hans Meyer, *Melliands Textilber*, 6, 737 (1925).

† Eichengrün, *Chemikerzeitung*, 51, 25 (1927).

‡ In case it has been saponified it burns similarly to viscose, cuprammonium or denitrated cellulose nitrate silk.

§ R. O. Herzog, *Die Kunstseide*, 9, pp. 7 et seq. (1927).

the whole subject is still to a great extent in the experimental stage; for all that, extremely interesting data are known, so that it appears necessary to discuss the matter here, more particularly as large industrial interests have taken up the question through the intervention of the Vereinigten Glanzstoffabriken* and Courtaulds, Ltd.,† who propose to operate the process on an industrial scale.

Lilienfeld‡ was the first to suggest the possibility of manufacturing artificial silk from cellulose ethers, in 1912. The conversion of cellulose into ethers is, however, still too expensive and the process has not been sufficiently developed. Either cotton, cellulose, or good sulphite pulp can be used as raw materials for the process. The conversion of this material into ethers is, however, impossible without further pre-treatment. Apparently, a considerable depolymerization of the cellulose complex is essential for its conversion into ether, which is carried out in presence of alkali by interaction of the cellulose with alkyl halide or alkyl sulphate. The reactions have been studied more particularly by Denham and Woodhouse,§ and also by Heuser and Hiemer.|| The fact that the cellulose or cellulose derivative changes into a water-soluble product before being completely converted into ether, appears to be ample evidence of deep-seated depolymerization. The highly alkylated ethers are alone insoluble in water, but they are soluble in an exceptional number of organic solvents, a fact which may also be considered to prove the deep-seated depolymerization of the cellulose. The ethers which are used are ordinarily cellulose ethyl ethers. Solutions of these substances can be converted into threads by either the wet or the dry spinning process, in a similar manner to solutions of cellulose nitrate or acetate.

Cellulose ether fibres have the advantage over all other artificial silk products, with the exception of undenitrated cellulose nitrate silk, that they are absolutely resistant to

* *Die Kunstseide*, 9, 481 (1927).

† *Die Kunstseide*, 9, 509 (1927).

‡ Austrian patent, 78,217.

§ *Zellulosechemie*, 1, 14, 22 (1920).

|| E. Heuser and N. Hiemer, *Zellulosechemie*, 6, 101, 125, 153 (1925).

water. They have the advantage over esters, and more particularly over cellulose acetate, which is easily attacked, of great chemical inertness, not only to water, but also to alkalies and acids.

The above-mentioned water-soluble products are more soluble in cold than in warm water, and are precipitated from such solutions by tannins in a similar manner to albumen. The exceptional property of inertness to water is, however, not common to all cellulose ethers and is, for example, not shared by the glycoll ether of cellulose, obtained by the interaction of ethylene oxide with that substance, according to German patent 363,192 of Elberfelder Farbenfabriken, probably in consequence of the free hydroxyl group which is still present in the glycoll residue.

Fibres of cellulose ethyl ether silk swell in hot zinc chloride solution, in concentrated hydrochloric acid, and in concentrated nitric acid. They can be dissolved in a large number of organic solvents, such as chloroform, aniline and benzyl acetate. Almost all organic solvents swell the material, even if they do not dissolve it. Apart from the patents of Lilienfeld, those of Dreyfus, of Bayer & Co., and of the Eastman Kodak Co., may be specially mentioned.

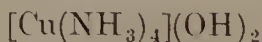
CHAPTER XIV

THE CUPRAMMONIUM PROCESS

Theoretical. The process depends on the solubility of cellulose in ammino-cupric hydroxide solution, which was already observed by Schweizer in 1857.* Such a solution is obtained if a solution of copper sulphate is precipitated with a small amount of ammonia, the precipitate filtered, washed, and dissolved in excess of ammonia.† If, on the other hand, an aqueous solution of copper sulphate is treated with an excess of ammonia, the solution mainly contains ammino-cupric sulphate



the bulk of which is converted by a large excess of sodium hydroxide solution only into ammino-cupric hydroxide



which is also known as cupric-tetrammino-hydroxide. If the ammonia is removed from these solutions, copper hydroxide is precipitated.

In the cuprammonium silk process as now carried out, the mixture obtained by adding sodium hydroxide solution to copper sulphate solution, including the precipitated copper hydroxide, is directly mixed with the cellulose. Under these conditions copper-sodium-cellulose is first formed, which may be assumed by analogy to contain the copper in the form of a complex group, similar to the form in which it is present in the sodium-copper glycerate



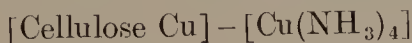
described by F. Bullnheimer.‡ If copper hydroxide is present in excess, as is usually the case, the copper-sodium-cellulose— $[\text{Cellulose Cu}]\text{Na}$ —may go into solution on addition of

* *Journ. f. prakt. Chem.*, 72, 109 (1857).

† Lunge-Berl, *Chemisch-technische Untersuchungsmethoden*, 7th Edition, 4, 502 (J. Springer, Berlin).

‡ *Ber.*, 31, 1453 (1898).

ammonia with formation of cupric tetrammine-cupric cellulose,



This view of the process may be assumed by analogy from the very complete investigations of W. Traube* on the reaction of polyhydroxyl compounds with cupric ethylene diamine hydroxide or with the copper oxide-ammonia compound of similar structure. (One ethylene diamine molecule replaces 2 ammonia molecules). If one first produces cupric tetrammine cellulose



according to Traube, and dissolves this compound in cupric tetrammine hydroxide, copper is removed from the latter compound with liberation of ammonia and is linked with the cellulose complex as in the above formula, with formation of soluble cupric tetrammine-cupric cellulose. This liberation of ammonia was previously observed by Linkmeyer.† The capability of a cupric tetrammine solution of dissolving further quantities of copper after the addition of a polyhydroxyl compound depends on the above-mentioned reaction.‡

In practice a process has been developed which will be described below, logically based on the above mentioned phenomena, according to which, in order to reduce the number of operations, the whole of the copper is added to the reaction mixture at starting.

Practical. PREPARATION OF THE CELLULOSE ; MANUFACTURE OF THE SOLUTION : PRECIPITATION BATHS. Cotton cellulose, in the relatively cheap form of linters, is almost exclusively used for the manufacture of cuprammonium silk. Cuprammonium cellulose solutions can also be manufactured from sulphite pulp, which is used in the form of thin tissue paper in order to ensure the maximum solubility ; but the silk produced with this material has not nearly as satisfactory an appearance and as good a handle as that prepared from cotton or linters.

* *Ber.*, 54, 3220 (1921) ; 55, 1899 (1922) ; 56, 268, 1653 (1923).

† German patent 183,557/1904.

‡ We may refer briefly here to the property of cupric tetrammine solutions and also of the corresponding cellulose solution, of absorbing atmospheric oxygen. An analogous property is possessed by solutions of sodium trithiocarbonate and of viscose.

The linters are first mechanically cleaned on carding machines, then carefully defatted by boiling under pressure with a dilute sodium hydroxide solution of $\frac{1}{4}$ to 1 per cent concentration, and then weakly bleached. The cellulose is then disintegrated in a pulp engine by a similar process to that described when dealing with cellulose nitrate.

The process used in practice for the manufacture of copper-sodium-cellulose and of the actual cuprammonium cellulose spinning solution is in general agreement with that described in French patent 249,841/1910, although it has undergone slight alterations here and there, such as are mentioned by H. Jentgen,* who describes the historical development of the cuprammonium silk process in its main phases.

The cuprammonium cellulose solution is produced substantially as follows: 155 kg. of pure crystalline copper sulphate are dissolved in a sufficient quantity of warm water at about 50° C., conveniently with stirring or in a suitably constructed dissolving apparatus, and the solution is then cooled to about 0° C. by addition of ice; 134 kg. of 35 per cent sodium hydroxide solution are then gradually added, with avoidance of rise of temperature. If the solution is kept sufficiently cold, a bright light blue precipitate of copper hydroxide is formed, which easily becomes dark coloured with separation of water if warmed. The precipitate, together with the supernatant liquid, is then mixed with 100 kg. of the prepared and well-beaten and disintegrated cotton for about 10 minutes in a pulp engine, at a temperature not exceeding 30° C.

The paste of copper-sodium-cellulose so obtained is freed from the main portion of the accompanying liquid in filter presses lined with cloth, and is then pressed in heavy presses at pressures of 200 atmospheres, in order to remove the liquid as far as possible, together with sodium sulphate in solution, which would exercise a coagulating effect on the solution subsequently to be obtained. Small amounts of copper, which are still present in the expressed liquor, settle quickly and are recovered. About 133 kg. of pressed residue is so obtained,

* *Faserstoff und Spinnpflanzen*, 6, 49 (1924).

which is thoroughly broken up in disintegrators (supplied, for example, by Werner & Pfleiderer, Cannstatt, and is then gradually dissolved, in a vessel provided with a stirrer, in 340 kg. of concentrated ammonia (sp. gr. 0.91), with the addition of a little ammoniacal bisulphite solution and of 1.8 kg. of acid potassium tartrate dissolved in ammonia, together with $32\frac{1}{3}$ litres of water. It is then continuously stirred in absence of air for about 5 hours, in which time it is dissolved. The solution is diluted, till it contains the required percentage of cellulose, by the addition of a liquid containing 86 parts of water, 3 parts of ammonia, and 20 parts of 35 per cent sodium hydroxide solution. It is then homogenized by stirring for about 10 hours. The solution which is usually employed contains from 8 to a maximum of 9 per cent of cellulose. The object of the addition of potassium hydrogen tartrate (which may be replaced by sugar) and of bisulphite (which is often replaced by hydrosulphite), is to protect the solution and the dissolved cellulose from oxidation, as it readily absorbs oxygen, as already mentioned.

The spinning solution is now ready, and is filtered at least three times through very fine iron or nickel gauze, and is then placed under vacuum for 12 hours in order to remove air bubbles, which would interfere with the spinning operation; the ammonia evolved during this evacuation process is recovered.

If the cotton has been replaced by wood pulp, the copper sulphate is precipitated as basic copper carbonate by the addition of sodium carbonate solution instead of sodium hydroxide; otherwise, the process is carried out as described above.

For spinning, multiple nozzles of nickel or copper are used, which have a width of aperture of 1 mm. for the stretch spinning process, which is now exclusively used.

Thick filaments, so-called "artificial horsehair," can also be produced in particularly good quality from the solutions just described.

As precipitation baths, solutions of acids, acid salts, alkalies and salts, and also pure water may be used, as all of these

either remove the ammonia necessary as a solvent, with precipitation of gelatinous copper cellulose, or cause simple colloidal coagulation. In the stretch spinning process, as now carried out, a gentle precipitation with alkali or pure water at 28° to 30° C. is alone used. The thorough recovery of the copper from the precipitated thread is carried out with dilute hydrochloric or sulphuric acid, immediately after the precipitation process.

Recovery of Chemicals. The cuprammonium process is considerably cheaper than the older cellulose nitrate process. This was particularly true at the time when it was introduced, as the recovery of organic solvents was in those days a rather difficult problem. In order to render the cuprammonium process economically sound, it is to-day necessary to recover the valuable chemicals, ammonia and copper, very completely.

In acid spinning baths the ammonia is immediately neutralized by the acid of the bath and fixed, whilst in aqueous spinning baths it is largely dissolved and so recovered; with alkaline spinning baths, on the other hand, a careful ventilation system must be provided in order to recover the ammonia, and for this reason the spinning machines must be enclosed in the same manner as when using organic solvents. In the stretch spinning process, which is almost exclusively used to-day, the enclosure of the machine is largely necessitated by purely mechanical reasons. The aspirated air containing ammonia is led through washers filled with acid, and the ammonia is greatly concentrated in the acid solution.

The recovery of the copper, which must in any case be removed from the spun thread, is also very important. When using acid spinning baths, a large proportion of the copper is dissolved by the bath, whilst when using aqueous and alkaline spinning baths the thread leaving the bath is carried over gutters before being wound, in which hydrochloric or sulphuric acid runs in counter-current to the product and dissolves the copper hydroxide which it contains.

Finished cuprammonium silk is not supposed to contain any copper, but it is always possible to distinguish it from other silks by the small traces of that metal which it contains.

By incinerating about 50 gm. of such silk, copper can always be detected in the ash. In the manner above described, about 70 to 80 per cent of the copper which is used can be recovered and returned to the process. An improvement in the method of recovering copper would introduce a further economy into the manufacture of cuprammonium silk, which it is only possible to produce to-day at a profit on account of the prices paid for it on account of its special qualities. It is manufactured on a large scale, particularly by the J. P. Bemberg A.G.

The cuprammonium silk at present marketed is distinguished from other artificial silks by the fineness of its fibres and by its appearance, which very closely approximates to that of real silk. For these reasons it has maintained a monopoly position for a long time. It is now, however, possible to obtain a product equal to cuprammonium silk in fineness not only by the acetate silk process, which is very expensive, but also by special modifications of the viscose process.

With regard to tensile strength when dry and when wet, cuprammonium silk has, however, not so far been equalled by any other product.

According to H. Jentgen,* the consumption of copper, ammonia and sodium hydroxide per 100 kg. of cotton is as follows for the various cuprammonium processes which have been used at one time or another.

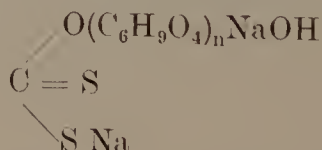
Process	Kg. Metallic Copper	Kg. Ammonia	Sodium Hydroxide Solution of 35 per cent by Weight
Use of metallic copper .	44.4	910	75.0
Copper hydroxide process with refrigeration .	41.8	634	160.0
Basic copper sulphate process .	41.5	650	63.3
Stretch spinning process .	39.0	338	170.0

* Loc. cit.

CHAPTER XV

THE VISCOSE PROCESS

The Theory of Viscose and Xanthate. By far the greater part of the artificial silk at present marketed is prepared by the viscose process. On account of the very high viscosity of its solutions, cellulose xanthate was called "Viscose" by its inventors, Cross and Bevan, who first prepared it in 1892. They identified the new compound, which they prepared, as the sodium salt of the dithiocarbonic acid ester of cellulose, and gave it accordingly the following formula—



This formula is still generally used to-day. The size of the cellulose complex varies in practice with the age and method of production of the viscose. The degree of facility with which viscose is salted out from its aqueous alkaline solutions depends on the size of that complex. The degree to which viscose can be salted out is generally described as the "degree of ripeness," and is determined technically by the well-known method of Hottenroth* by measuring the number of cubic centimetres of 10 per cent ammonium chloride solution which are necessary in order to coagulate 20 gm. of viscose which have previously been diluted with 30 gm. of water. Apart from the alkali contents and viscosity of the viscose under examination, the temperature and the rate at which the determination is carried out are controlling factors. The contents of trithiocarbonate also influence the result. The viscosity of viscose is dependent, amongst other factors, on the contents of alkali. Alkali (NaOH) has a peptonizing action on the xanthate, and also retards the ripening process. In

* *Chemikerzeitung*, 39, 119 (1915).

this case, as usually in the peptonization of colloids, there is an optimum degree of concentration. The viscosity of the freshly dissolved viscose at first decreases with time, as has long been known in practice, and then increases with increasing ripeness until the viscose finally coagulates. Apart from the contents of NaOH and of cellulose, the rapidity of this process is largely dependent on the temperature and on various additions and impurities.* Mukoyama obtained the unexpected result that the surface tension of viscose solutions was somewhat lower than that of water or of alkali solutions of the same concentration, and was independent of the age of the viscose. When viscose is always produced by the same process as is, of course, usual in works in continuous operation, Hottenroth's method of testing is very useful. Mukoyama† found that fresh viscose solutions, which were not coagulated by 10 per cent ammonium chloride solution, showed a maximum viscosity on the addition of a number of cubic centimetres corresponding to the degree of ripeness, and that the same viscose in a condition of greater ripeness shows the same viscosity if the quantity of ammonium chloride corresponding to this degree of ripeness is added. (The latter observation appears to be somewhat uncertain on account of the great alteration in the viscosity.) The determination of the coagulation caused by sodium chloride solutions of definite concentration is also used in practice as a method of examination.

Apart from the determination of the so-called "degree of ripeness," another method of investigation is employed in order to determine the size of the cellulose complex within the bracket in the above formula. Cross and Bevan already showed that 2 molecules of xanthate unite to form dixanthate by the action of iodine, with formation of sodium iodide; the amount of iodine absorbed by this reaction can easily be determined by titration. For this purpose the viscose solution, which is usually alkaline, must first be neutralized. This neutralization must, however, be carried out with the greatest

* See investigations carried out by Takayoshi Mukoyama at the suggestion of W. Ostwald, *Kolloid-Zts.*, 41, 42 (1927); 42, 354 (1927).

† *Koll. Zts.*, 43, 349 (1927).

care, as acids, and more particularly mineral acids, immediately decompose the xanthate with reformation of cellulose hydrate.

According to H. Jentgen,* the determination is carried out by decomposing the sodium trithiocarbonate, always present as an impurity, by means of mineral acid, thus regenerating cellulose hydrate, and by titrating with iodine the hydrogen sulphide which is so liberated. For this purpose the viscose solution is diluted ten-fold, and 25 c.c. of the solution so obtained are diluted with 2 litres of water and placed in a 3-litre flask closed with a rubber stopper; 25 c.c. of normal sulphuric acid are then added through a separating funnel, by means of slight excess pressure produced, for example, by blowing with the mouth. The whole is then shaken, and after 10 to 15 minutes an excess of 0.1 N. iodine solution is also introduced into the closed flask by air pressure through the separating funnel; after thorough stirring, the excess of iodine is titrated back.

If one succeeds in decomposing the trithiocarbonate without affecting the xanthate, the sum of the xanthate and sodium trithiocarbonate can be determined by further titration with iodine, which forms dioxanthate with the xanthate, with corresponding removal of iodine; from the difference of the two determinations the amount of iodine consumed in the formation of dioxanthate can be found. The magnitude of the cellulose complex in the above-mentioned xanthate formula can be deduced if the cellulose contents of the viscose are known; this can be found by decomposing a definite amount of viscose, washing and drying. For the determination of the trithiocarbonate, it is sometimes wrongly decomposed by the addition of 25 c.c. of normal acetic acid to the above-mentioned quantity of viscose; the determination is otherwise carried out in exactly the same manner. F. Dietler† found, however, that formic acid also decomposes xanthate with formation of cellulose hydrate. This is also the case with much weaker organic acids, including acetic acid,‡ and for this reason Faust, Graumann and Fischer§ proceed by using for the decomposition of the trithiocarbonate

* *Laboratoriumsbuch für die Kunstseide- und Ersatzfaserstoffindustrie* (W. Knapp, Halle, 1923), p. 55.

† U.S. patent 1,073,891/1911; German patent 254,525/1911 (lapsed).

‡ F. Westhoff, Dissertation, Hanover, 1911.

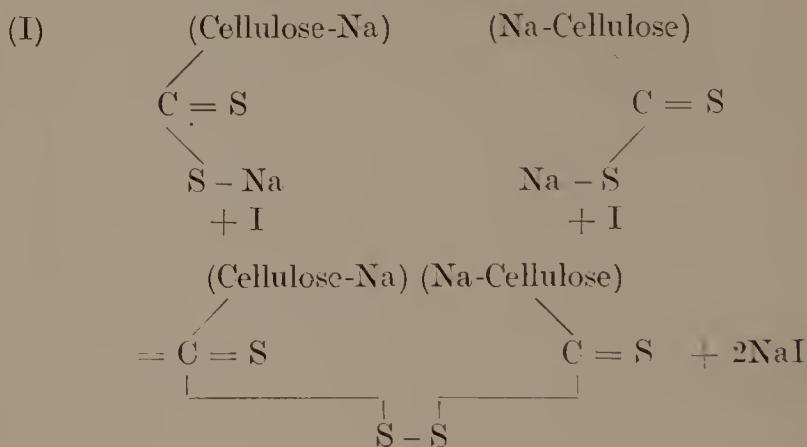
§ *Zellulosechemie*, 7, 165 (1926).

one more drop only of normal acid than the amount of acetic acid required for neutralization, as previously determined.

Further investigations have also shown that it is desirable to add the iodine which accomplishes the dixanthate formation as rapidly as possible after neutralization, as viscose is not very stable in dilute neutral solutions containing salts. Different results are obtained if one adds the iodine 3, 6, 10 or more seconds after neutralization. If, however, the determination is always carried out in a uniform manner, for example, by always adding the iodine 30 seconds after completed neutralization (a period which can easily be maintained by an experienced assistant), values are obtained which are easily reproduced and which are comparable, although they must not be considered to be absolutely correct. The rate of decomposition of viscose through the action of acetic acid has an essential bearing on the value obtained, as has been shown by detailed investigations which have not yet been published.

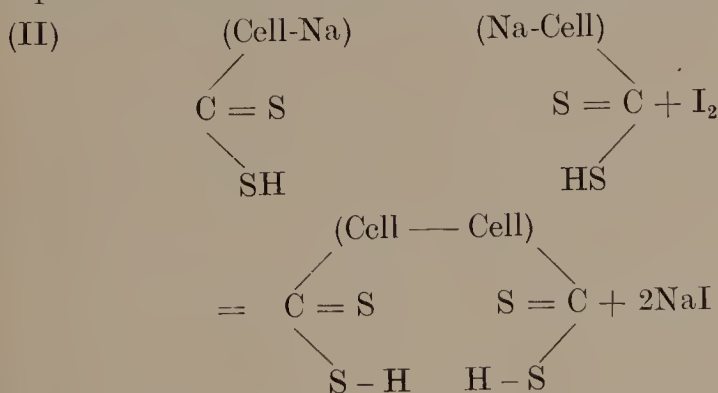
The above determination, with the modification described, must therefore be considered as a merely conventional determination. In effect, with uniform manipulation, more particularly regarding the quantities of acid used and the periods during which this is allowed to act, it gives reproducible results, which are therefore valuable in practice and which enable an opinion to be formed on the uniformity of the condition of the viscoses investigated. From a purely scientific standpoint, difficulties occur; on decomposing viscose with mineral acid trithiocarbonate is formed by the by-reaction ($4\text{NaOH} + 3\text{CS}_2 = 2\text{Na}_2\text{CS}_3 + \text{H}_2\text{CO}_3 + \text{H}_2\text{O}$) and is decomposed with formation of carbon disulphide and hydrogen sulphide, whilst the xanthate forms carbon disulphide and cellulose only. By determining the quantity of H_2S by titration with iodine, the sulphur in the trithiocarbonate can therefore be calculated. On the other hand, on neutralizing with acetic acid the sodium trithiocarbonate present as a by-product is decomposed in the manner indicated above, whilst the cellulose xanthate remains undecomposed with the above reservation, so that in this case the iodine which is added reacts with the hydrogen sulphide formed from the trithiocarbonate, as

explained above, and further iodine is used for the formation of dixanthate according to the following equation—

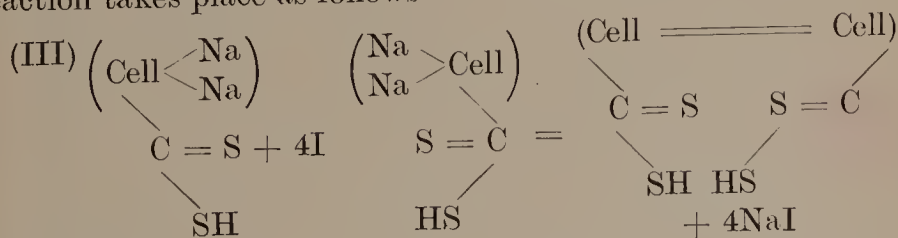


If the quantity of iodine which reacts with the hydrogen sulphide, obtained by the decomposition with mineral acid, is deducted, one obtains the quantity of iodine used according to the above equation for the formation of dioxanthate, which determination is the basis of the above-described phase determination, that is, of the determination of the $\text{C}_6\text{H}_{10}\text{O}_5$ groups which are combined in viscose with one xanthate group $-\text{CS}(\text{SNa})$. In this case, also, the quantity of sulphur can, of course, be calculated on the basis of the above equations; thus the quantity of sulphur contained in the viscose and in its by-products can be determined by the aid of these two decompositions and iodine titrations. If, however, one of the other known methods of determining sulphur is employed and used—for example, complete oxidation with hydrogen peroxide or similar oxidation methods—the surprising result is obtained that in this manner only about two-thirds as much sulphur is found as by the above-mentioned methods. This is a proof that the assumed reactions for the decomposition by acid and titration with iodine are not in complete accordance with the actual facts. This furnishes a further reason for considering this method of investigation, for the present, as a merely conventional method, the complete elucidation of which remains a scientific problem of the future.

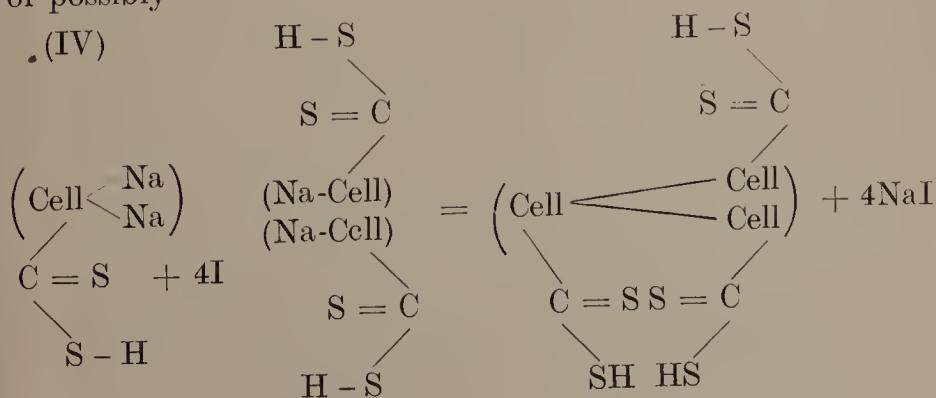
If one assumes that the iodine does not remove the alkali combined with sulphur, as this may already have been removed during neutralization, with formation of free xanthic acid, but that, on the other hand, the sodium combined with the cellulose complex is attacked according to the following equation—



one may further assume, following this line of argument, that several—for example, 2—sodium atoms are combined to form alcoholates with the cellulose complex of 1 xanthate molecule, and that these react with the iodine, so that the reaction takes place as follows—



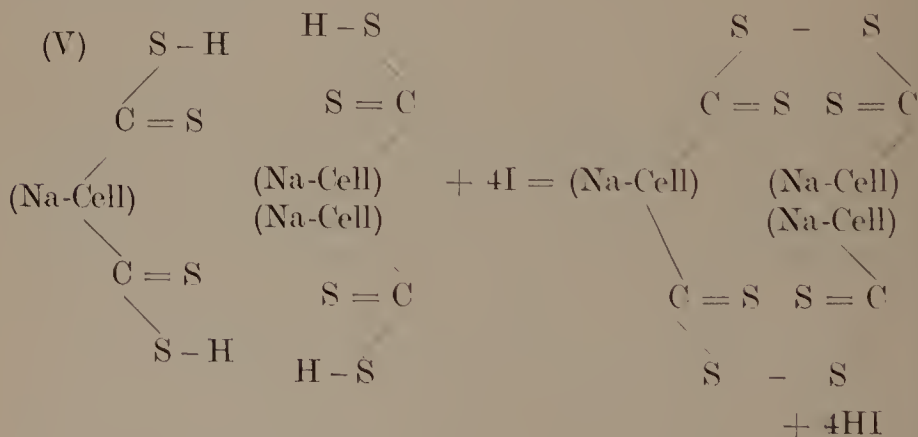
or possibly—



so that 3 xanthate molecules interact to form one larger molecule.

It is, of course, also possible that a mixture of various forms of xanthate is present and that, for example, in one portion of the xanthate molecules more than one hydroxyl group of the cellulose has been converted into xanthate.

On xanthation with a large excess of carbon disulphide, decomposition with acetic acid and immediate addition of iodine, a precipitate containing cellulose is obtained in the reaction vessel, the formation of which might, for example, be explained by supposing the action of the iodine and the formation of dixanthate to be directed to the atom of sulphur, as in equation I—



One may, of course, easily assume that more than 3 molecules of xanthate are combined in this manner, if, for example, 2 molecules each containing 2 xanthate groups are coupled with a further group, whilst further xanthate molecules are coupled to this other group. Such large aggregates might differ greatly in solubility from dixanthates of the type suggested in equations (I) to (III).

Apparently problems are here involved which require scientific investigation. The great stability of the dixanthate and of the other forms described above, possibly those of equations IV and V, compared with that of the normal xanthate of viscose, is remarkable.

Sulphite pulp is quite generally used for the manufacture of viscose silk, whilst the pulp obtained by the soda process, usually from very resinous pine wood, has so far been found useless for the manufacture of artificial silk. The use of cotton or linters appears to be justified in places only where these can be obtained at a cheaper price, or where good sulphite pulp is unobtainable.

The various qualities of sulphite pulp are by no means of equal value for the manufacture of artificial silk, and only pulp of artificial silk quality, from a sulphite pulp works of long experience, can be safely used for the manufacture of a uniform and utilizable viscose silk.

The Manufacture of Viscose. (a) *Alkali Cellulose.* For the manufacture of viscose, wood pulp in the form of sheets or boards, dried as already described, must be mercerized in 18 per cent sodium hydroxide solution. Mercerization with an alkaline solution of potassium hydroxide does not lead to the subsequent production of a cellulose xanthate of good solubility, which can readily be filtered, and potassium hydroxide cannot, therefore, be used. The degree of swelling of wood pulp in caustic potash solution is entirely different from that in caustic soda.

Caustic soda solution is supplied in tank wagons in concentrations of about 37 per cent by weight. In winter it is advisable to order solutions of 30 to 32 per cent concentration, in order to avoid freezing. The concentrated 37 per cent solution offers the advantage that the quantities of sodium carbonate, which are in any case present, are very small, as the solubility of sodium carbonate in the concentrated solution does not exceed 0.5 per cent calculated on the NaOH.

The solution must be as free from iron as possible, for which reason it is allowed to settle for a considerable time in the artificial silk works. It is advisable to dilute before settling, so that the iron hydroxide may readily settle. Some works use solid caustic soda, which is dissolved in a special plant. A very practical form of installation for this purpose was described, for example, by Czapek,* (Fig. 49). In this apparatus,

* *Zts. f. angew. Chem.*, 38, 841 (1925); German patent 414,852/1923.

in which no mechanical stirrer is required, the difference of the specific gravities of water and of concentrated caustic soda solution, or of dilute and concentrated caustic soda solutions, is used to promote circulation during the process of solution. A solid block of sodium hydroxide is placed in a vessel with a perforated floor. This vessel is inserted in a larger vessel which surrounds the former as a mantle. The whole apparatus is filled with water within and without. The

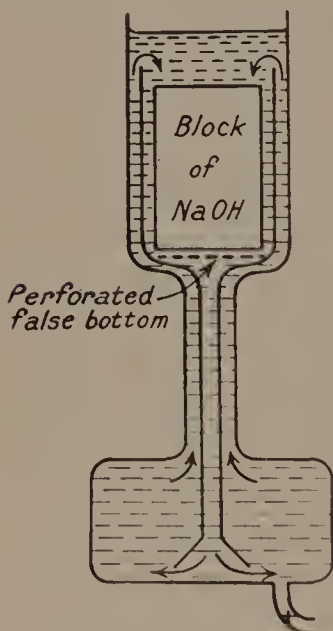


FIG. 49. CZAPEK'S DISSOLVER

heavy solution sinks through the false bottom into the outer vessel and forces the water in the latter upwards so that it falls over the upper rim of the inner vessel and on to the caustic soda. The width of the lower, funnel-shaped opening of the inner vessel shown in Fig. 49 can be regulated, which is an important point. In this plant, an unbroken block of 300 kg. of caustic soda can be dissolved in one to two hours. The apparatus is supplied by W. Salge & Co., Berlin, W.S.

O. Funke* also describes a suitable plant of a somewhat different kind for dissolving solid caustic soda.

Disintegrated wood pulp is mercerized in simple iron dipping tanks, whilst sheets are mercerized in a so-called dipping press, such as is described in German patent 270,618. Fig. 50 shows such a press at the moment of completion of the pressing operation.

Cellulose sheets are charged into the dipping vat *A* in a vertical position, being separated from one another by vertical perforated metallic plates, and the vat is then charged with sodium hydroxide solution. After dipping for one to two hours at the ordinary temperature, or a somewhat lower temperature, the piston-rod *G* and the piston-head *F* which it carries, are forced

* German patent 449,986/1923.

in the direction of the arrow *H* by the hydraulic pump *B*, and the alkali cellulose which has already been formed is compressed by the piston until its weight amounts to three times that of the original dry pulp, the press liquor being expelled. The presses are frequently provided with weighing machinery, as the uniformity of the pressure employed does not necessarily guarantee a uniform content of wood pulp in the product, especially when wood pulp of varying qualities is used, as these may swell by different amounts. After pressing is complete, the piston is withdrawn and the alkali cellulose is conveyed into movable containers and removed to the disintegrators (Fig. 52, page 157).

Fig. 51 shows a modern dipping press constructed by M. Häusser, Neustadt a. d. Hardt, a firm well-known for the supply of such apparatus. The apparatus shown has a capacity of 100 kg. of pulp. Instead of constructing the press so that the counter-plate which withstands the pressure can be raised upwards as in *E*, Fig. 50, Häusser's press is furnished with a cage as shown in Fig. 51, into which the whole of the charge of pulp is pressed by the piston, together with the diaphragms shown in the illustration. Both these and the piston travel in guides, which prevent the sheets of pulp from being distorted and expelled from the press. Pulp sheets are used of dimensions 80×62 cm. or 82×62 cm. The cage can be lifted by a travelling crane as shown in the illustration, and emptied into a truck for further disposal. The firm also constructs presses for premises which are not high enough for a travelling crane, provided with a trap door permitting discharge in a

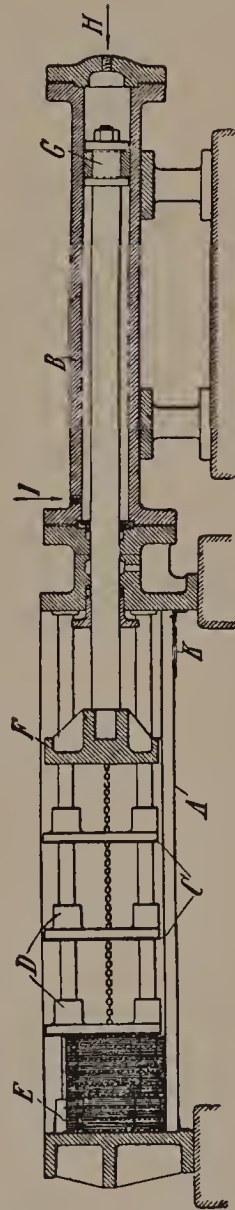


FIG. 50. DIAGRAM OF DIPPING PRESS
(Ger. pat. 270618)

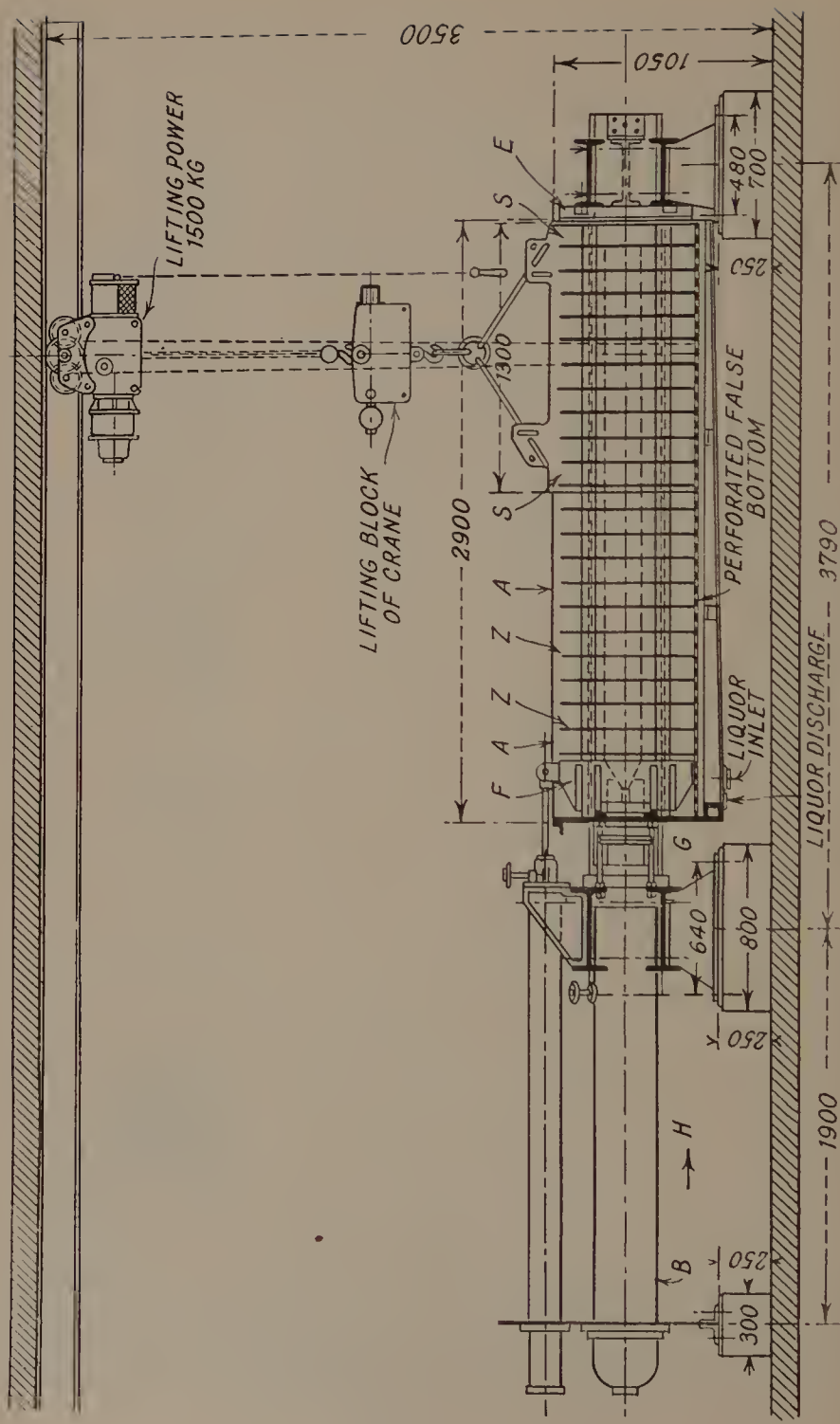


FIG. 51. HYDRAULIC MERCERIZING PRESS
Capacity, 100 kg. cellulose. Maximum pressure, 70 tons at 275 atm. (M. Häusser, Neustadt)

downward direction. When using this press the finished mercerized product can, of course, only be weighed in the transporting truck. Details and dimensions will be clear from the figure. The economic advantage of the dipping press has to-day been clearly demonstrated.*

Such presses are constructed for cellulose charges of 50, 100 and 200 kg., and the output is about 10 to 12 charges per 24 hours.

In mercerizing previously disintegrated cellulose by the method already referred to, the contents of the dipping pot are discharged into a centrifuge in the same manner as after nitration, and the main quantity of the liquor is thus removed; the alkali cellulose, which still contains too large an excess of caustic alkali solution, is removed from the walls of the centrifuge and reduced to the desired weight in a neighbouring press provided with a weighbridge. This method offers the advantage that the press liquor, which is especially impure, can be collected separately. Compared with presses, the power requirements of centrifuges are very considerable. In presses the last portions of the press liquor can, of course, also be collected separately, as is now usual.

The press liquor—also known as “yellow liquor”—contains less alkali than the dipping liquor originally used, as the pulp removes alkali from the liquor with formation of alkali cellulose, and water is thus liberated. Moreover, the press liquor, as already indicated, is contaminated by organic substances (pentosans and hexosans), which are always present in sulphite pulp. It is, therefore, important to use a pulp containing as little as possible of such impurities, that is, with a high percentage of α -cellulose. The uniformity of the contents of these impurities is, however, still more important for the manufacturer. Pulps intended for artificial silk manufacture usually contain 8 to 14 per cent of such impurities, that is, 86 to 92 per cent of α -cellulose. Especially purified pulps with a higher percentage of α -cellulose are also now supplied. We may

* O. Faust, *Die Seide*, April, 1928.

The lettering of Fig. 51 corresponds to that of Fig. 50. In addition, the sieve plates between the wood pulp sheets are designated by *Z* and the removable cage by *S*. The hydraulic mechanism for withdrawing the piston after pressing is completed is situated above the pressure pump *B*.

refer specially here to the *a*-cellulose of the Brown Co., prepared by Richter's process,* which contains about 94 per cent of *a*-cellulose, and consequently supplies a considerably purer press liquor. This product, which is prepared from sulphite pulp and has, therefore, the same properties, cannot, however, be used in the viscose silk industry, owing to its high price. The mercerization process is accompanied by a slight development of heat. (See "Heat of Swelling," page 57.)

The press liquor is partially re-utilized after regeneration with freshly prepared caustic alkali solution. Care must be taken that the contents of the above-mentioned organic impurities do not reach too high a concentration. To avoid this, a certain proportion of the waste liquor is always rejected by artificial silk works. A number of processes for purifying these liquors have become known, but appear to have found but little practical application,† with the sole exception of the process of Leonardo Cerini.‡ This is an osmotic process of purification which is operated continuously on the counter-current principle, and in which the reduction of the concentration of the liquors is small, and amounts to 1 to 2 per cent only.

The pressed alkali cellulose must now be disintegrated for further treatment. The disintegrators are large kneading machines, such as the one shown in Fig. 52. The rotating blades of this machine revolve at varying speeds, and are provided with teeth which engage with counter-blades in the disintegrator and reduce the alkali cellulose to a fine, flocculent mass in from 1 to 2 hours. These disintegrators are frequently provided with cooling devices in order to prevent an injurious rise of temperature.

The disintegrators can be tipped, as shown in the figure, and are by this means emptied into vessels of sheet metal, which are now ordinarily conveyed to the ripening chamber for the production of so-called "ripened" viscose. They remain in this chamber 3 to 4 days at a temperature of about 20° C. This ripening process causes an increased degree of uniformity

* George A. Richter, U.S. patent 1,643,355; French patent 621,412/1926.

† A. Sander, *Die Kunstseide*, 9, 12 (1927).

‡ *Giorn. di. Chim. Ind. ed. Appl.*, 8, 227 (1926); Italian patent 245,816/1926; see also H. Jentgen, *Kunstseide*, 8, 298 (1926).

of the product and a considerable reduction of the viscosity of the viscose produced from the same, compared with that produced from unripened alkali cellulose. The temperature is of great importance for this ripening process. Excessive temperatures of 30° and over are not desirable. Atmospheric oxygen is absorbed during the ripening process. (See pages 6 and 7.)

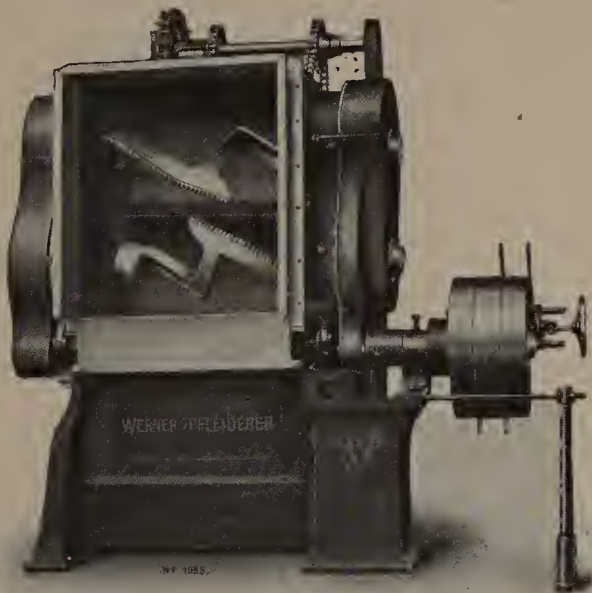


FIG. 52. DISINTEGRATOR FOR ALKALI CELLULOSE
(Werner & Pfleiderer)

Xanthation. After ripening, the alkali cellulose is treated with carbon disulphide in so-called xanthation churns for the manufacture of xanthate. 30 to 40 per cent of carbon disulphide is employed, calculated on the quantity of dry wood pulp.*

The xanthation churns (Fig. 53) may, for example, have a capacity of 1000 litres, in which case each charge consists of 300 kg. of alkali cellulose, equal to 100 kg. of dry pulp. They are usually provided with a water jacket, as the reaction is

* According to Austrian patent 105,031/1926 (British patent 212,865 and German patent application 257,661/120/1923), L. Lilienfeld employs a considerably lower proportion of carbon disulphide and intensifies the action, more particularly of the sodium hydroxide on the cellulose, by the employment of low temperatures down to -25° C.; but it is difficult to obtain viscoses which can be filtered by the process described by him.

exothermie, and excessive temperatures above 30°C . may easily occur, particularly if strongly ripened alkali cellulose is used. The supply and withdrawal of cooling water takes place through the hollow trunnion at *B*. *A* is the measuring vessel for carbon disulphide, with sight glass and scale. The carbon disulphide supply pipe is provided with a sight glass, and suitable provision is made for the addition of the carbon disulphide and the removal by suction of the reaction gases.

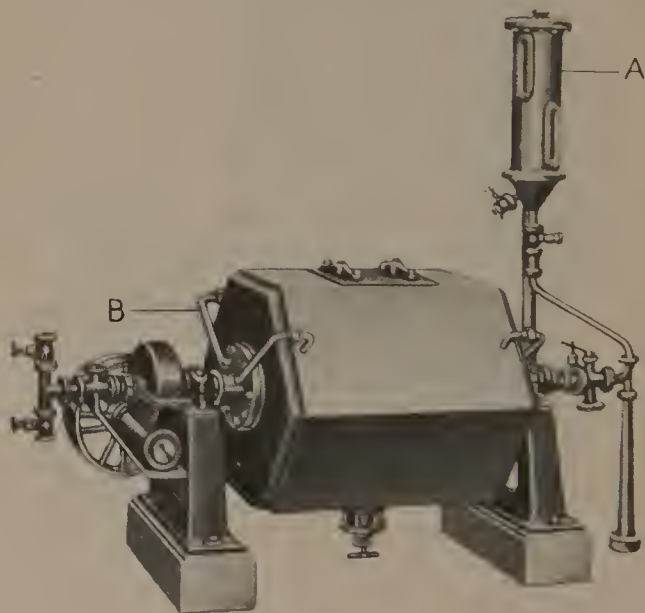


FIG. 53

The churn is driven by helical gear or by gear wheels. The water jacket is constructed of sheet iron, whilst the other parts are usually of cast iron. All parts are readily accessible, and can easily be taken apart. The drums must be tested under pressure in the shops in order to detect any leakages, which would entail danger of explosion. The carbon disulphide, which is conveyed to the measuring vessel *A* from the storage tanks by means of compressed air, passes into the interior of the xanthation churn under its own head. A uniform distribution of the carbon disulphide is ensured by the use of a delivery tube with small outlet perforations.

The white alkali-cellulose gradually attains a reddish brown

colour during the xanthation process, with simultaneous rise of temperature. The temperature should not exceed 30°C ., and the cooling must be correspondingly regulated. The whole xanthation process lasts for 3 to 4 hours, or sometimes less, and is finished when on viewing the reaction mass through the sight glass it is observed to have attained an orange colour. The added carbon disulphide has then been absorbed, which fact is also shown by the formation of a vacuum within the churn. It is a curious fact that this orange colour should be generally recognized in technical practice as an indication of the end of the xanthate formation, as it actually depends on the formation of sodium trithiocarbonate as a by-reaction, and is not to be ascribed to the formation of the xanthate itself. The latter, if, for example, it is freed from trithiocarbonate by washing with methyl alcohol, has a very light, greenish-yellow colour only, particularly in solution, whilst the alcohol acquires a dark brown to yellow colour. However, the method of determining the end of the reaction by the colour, which is quickly and correctly learned by every workman, has been found satisfactory in practice. With uniform methods of working, formation of the trithiocarbonate is also more or less uniform, and the reliability of the method depends on this fact.

A fact which is more troublesome in practice is the frequency with which the viscous reaction mass balls together to form spherical aggregates varying in size, the inner portions of which cannot be satisfactorily xanthated, or only xanthated with difficulty, and which must, moreover, be disintegrated before they are introduced into the dissolving tank, as during solution they form large lumps, the outer portions of which are slimy and tough, and the inner portions of which are not easily penetrated by the liquor; these render the process of solution very difficult. In well-conducted works the formation of these lumps is largely avoided. The reaction product, the xanthate, is tough and plastic, and can be rolled out to skin-like films, particularly after being ripened for several days; these films can be reconverted into cellulose and then form membranes with very useful properties.*

* O. Faust and H. Vogel, German patent 392,371.

Viscose Solution. In order to dissolve the xanthate and thus produce actual viscose, the xanthation churns, which are usually located directly above the dissolving tanks, are opened, the opening is turned downwards, and the reaction mass which falls out is passed through a sieve or grating, which serves to disintegrate the lumps formed during xanthation, into the primary solution tank, which is charged with dilute caustic soda solution. This tank may be vertical or horizontal, and is provided with a stirrer. The solution of the xanthate requires several hours. The cellulose contents of the solution are usually adjusted to about 8 per cent and the sodium hydroxide contents to about the same figure. In so-called "unripened," viscose, made from unripened alkali cellulose, a lower percentage of cellulose is used on account of the increased viscosity.*

After solution is almost complete, the thick viscous liquid is pumped into the final solution tank, passing through a so-called viscose disintegrator. Fig. 54 shows a disintegrator constructed by F. August Neidig, Mannheim, which is protected by a German registered design.

These disintegrators are provided internally with several perforated grinding discs, which are alternately rotary and fixed, between which the viscose is forced by a pump. Behind the perforated grinding discs there is situated a grinding plate, which is pressed by a spring on to a fixed annular surface; in consequence of the large diameter of this plate, it allows the whole of the viscose to pass, even if the pressure of the liquid suffices to raise it above its seating through a distance of a few tenths of a millimetre only. Thus, at the edge of this plate, an annular slot is formed, about two-tenths to three-tenths of a millimetre wide, but of very considerable circumference, through which the whole of the viscose has to pass. This ensures that even the smallest lumps of viscose, which may still be present after their passage through the perforated discs, must be disintegrated before they pass through the slot. The viscose is, therefore, necessarily converted into a perfectly

* See, for example, German patent 389,394 of Glanzfäden A.G. (now Vereinigte Glanzstoffabriken, Elberfeld).

homogeneous fluid by a single passage through the machine. This disintegrator does not itself convey the solution, which has to be passed through it at a pressure of from 2 to 4 atm., according to its quality.

The lateral thrust exerted on the rotary discs by the pressure at which the viscose is supplied, is taken up by an external adjustable ball-bearing, which is contained in a casing and runs in grease, and does not come into contact with the viscose.

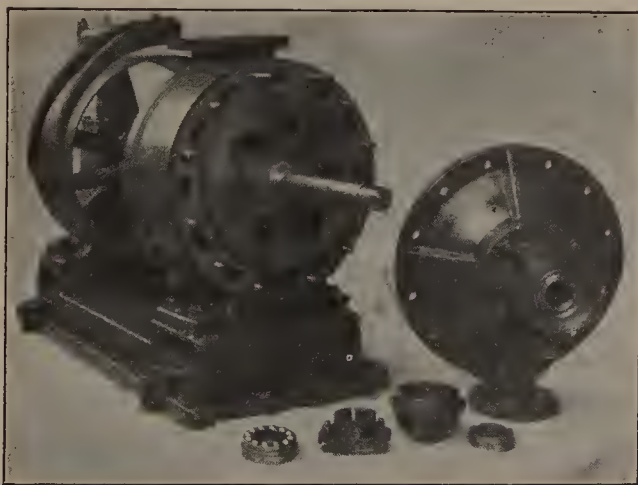


FIG. 54

Owing to the chemical character of viscose, precautions are taken to prevent even the smallest amount of heat from being developed by the disintegrating process, and the disintegrator is made sufficiently capacious and is provided with a cooling jacket. As is very often the case with lyophilic colloids, this powerful mechanical treatment results in a reduction in the viscosity which is, no doubt, attended by a certain reduction in size of the micellae.

From the disintegrators the viscose passes to the secondary solution vat, in which it is exposed to vacuum in order to remove the air bubbles. It is simultaneously stirred to promote admixture with a further quantity of water. If the viscose is to be spun in an unripened condition, it passes from this vessel, after very careful filtration, to the spinning tank, where it

is once more subjected to vacuum in order to remove as far as possible any bubbles, which have a very harmful effect on the spinning process.

If the viscose is to be ripened, this process, which is also known as "ageing," takes place at this stage.

The Ripening of Viscose. The viscose solution is further homogenized in the secondary solution tanks and also in the stirring vats, and is then filtered in the usual manner through a filter press, from which it is conveyed to a ripening tank placed in the so-called "viscose cellar." Specially constructed gear-wheel pumps are usually employed for this purpose, and are supplied, for example, by F. August Neidig, Mannheim.

Fig. 55 shows the arrangement of a complete battery of viscose tanks, consisting of three pre-treatment and three operating tanks. A filter press is inserted in front of each pre-treatment tank, and the supply piping is so arranged that they can be used alternatively when one or the other is temporarily out of use in order to be cleaned. The viscose tanks can all be subjected to air pressure of 6 atm. or to vacuum, and the supply and discharge pipes can be cut off from the individual kettles by suitable cocks or valves. Each tank is provided with a manometer and vacuum-meter, a manhole and sight-gauge, with discharge cock. They are so arranged that they can alternately be exposed to pressure and vacuum. The figure shows the arrangement in detail.

The temperature in the ripening cellar is maintained at a definite point, and the period of ripening usually extends from several days to one week. The ripening of viscose, which is frequently omitted in the more modern processes*, has for its object the conversion of the spinning solution into a condition in which it may coagulate as thoroughly as possible. During the ripening period the viscose increases in the ease with which it can be coagulated, and the ripeness value (ammonium chloride value by Hottenroth's method, see page 144) becomes steadily lower. Most works which use ripened viscose, work at an ammonium chloride value between 6 and 12, that is, 6 to 12 c.c. of 10 per cent ammonium chloride solution

* German patent 389,394.

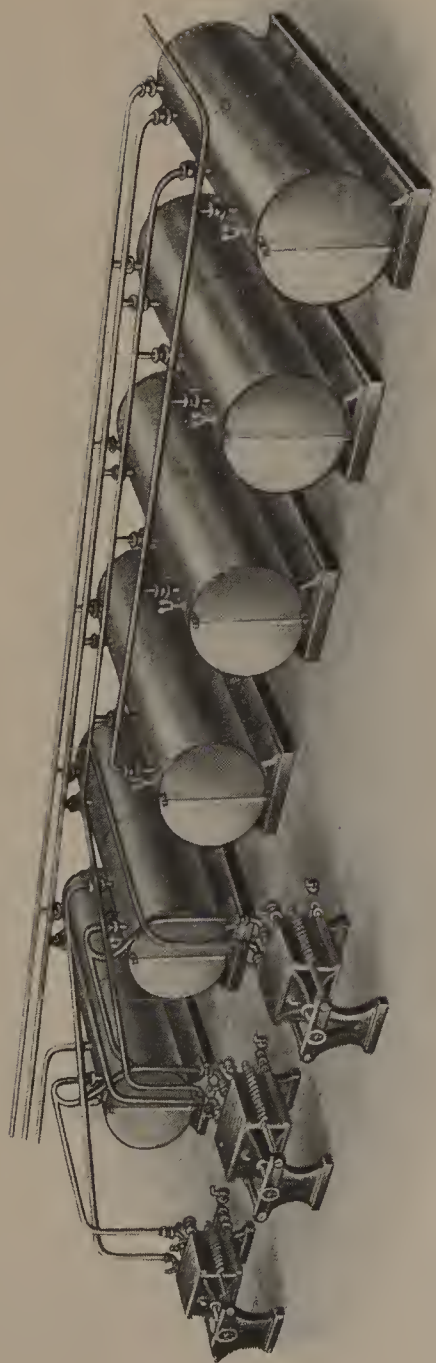


FIG. 55. BATTERY OF VISCOSE TANKS WITH FILTER-PRESSES

coagulate the viscose when added to the specified amount at the specified degree of dilution.

The ripening process is accompanied by an increase of the number n of the cellulose complex in the xanthate.* In a well-ripened viscose, about three $C_6H_{10}O_5$ complexes are present in the portion enclosed in the brackets in the formula, whilst in unripened viscose this complex is considerably smaller.

During the ripening process, the viscose is de-aerated repeatedly by the application of vacuum in order to remove air bubbles as completely as possible from the material, as these are injurious when spinning.

During the ripening process, carbon disulphide is liberated, as is obvious from the equations given above, in consequence of the enlargement of the cellulose complex, and reacts with the excess of sodium hydroxide with formation of trithiocarbonate.

It has not yet been ascertained with certainty whether during the ripening process the cellulose complex of individual xanthate molecules is actually enlarged at the expense of other xanthate molecules, or whether liberated cellulose complexes are simply held in solution by the action as a protective colloid of the xanthate itself;† a further hypothesis is also possible which is mentioned below. When a thread of artificial silk is precipitated with mineral acid, which certainly immediately entails the formation of cellulose hydrate, the precipitated product is at first still soluble in water, although it undoubtedly no longer consists of xanthate. In our opinion the molecule, or particle of xanthate, must be considered as a micella, possibly as shown in Figs. 56A to 56D, in which the units shown as ellipses are to be considered as individual cellulose molecules, or perhaps better as elementary crystals or individual groups, and the structures drawn in the form of T's are to be considered as xanthate residues.

The cellulose micella‡ consisting of several individual

* See Figs. 56A-56D.

† Berl, *Zellulosechemie*, 7, No. 10 (1926).

‡ The individual cellulose micellae may according to the hypothesis of K. Freudenberg be considered as built up of individual glucose chains with oxygen bonds, whilst the individual chains at least when dissolved are orientated in a very variable manner. Cellobiose chains are also possible. (K. H. Meyer and H. Mark, *Ber.*, 605 (1928).)

particles or individual groups, contains either a portion of its cellulose molecules in xanthated form (Figs. 56C and 56D) or the whole of them may be xanthated (Figs. 56A and 56B), in which case some of them may even contain more than one xanthate residue. The remaining non-xanthated particles, in cases 56C and 56D, are maintained in solution by the others. Assuming the same quantities of combined carbon disulphide,



FIG. 56A. FRESH VISCOSE
from unripened alkali cellulose
(so-called "unripened viscose")



FIG. 56B. FRESH VISCOSE
from ripened alkali cellulose



FIG. 56C. RIPENED VISCOSE
from unripened alkali cellulose



FIG. 56D. RIPENED VISCOSE
from ripened alkali cellulose

The above figures illustrate a conception of the condition of dissolved micellae, to which the assumption of K. H. Meyer and H. Mark (*Ber.* 61, 607 (1928)), that "micellar forces" induce crystallographic structure, does not apparently apply. The gelatinizing action of the solvent destroys the crystallographic structure.

a fresh xanthate micella contains more xanthate residues combined with the cellulose molecules than a ripened xanthate micella, which loses these groups by saponification and finally coagulates when insufficient xanthate groups adhere to the micella to maintain it in solution. According to the amount of carbon disulphide which has been used (for a condition of equilibrium has apparently to be attained), a cellulose micella may contain one xanthate group for less than one cellulose molecule, for each molecule or for more than one molecule of $C_6H_{10}O_5$. When, however, larger quantities of carbon

disulphide are used, the simultaneous formation of considerable quantities of trithiocarbonate cannot be avoided, nor a further formation of trithiocarbonate during ripening, which exercises a salting-out action, as was shown by Heuser and Schuster.*

If one starts with ripened alkali cellulose, the cellulose micella contains fewer individual cellulose molecules (Figs. 56B and 56D) than when unripened alkali cellulose is used (Figs. 56A and 56C), and this fact, together with a certain degree of chemical disintegration of the cellulose during ripening, explains the lower viscosity compared with that of cellulose from unripened alkali cellulose.† This explanation is in good accordance with the original suggestions of Cross and Bevan‡ and with those of Zart and Mönkemeyer.§

It is also possible that the individual constituents of the micella, which are not uniformly orientated, according to my investigations, and which do not become uniformly orientated when the viscose solution traverses narrow tubes, are so coupled with one another that on stretching the micellae at the moment of coagulation a uni-directional effect is produced of a more or less extensive character, which then shows itself by double refraction in polarized light and by the production of a more or less definite X-ray fibre diagram. It is conceivable that such fibre diagrams should be less definite when ripened alkali cellulose is used, with essentially smaller micellae, than when unripened alkali cellulose is used, in which the number of the particles which are orientated by the stretching process is certainly larger.

This process in the manufacture of viscose, which is generally referred to as ripening, definitely distinguishes viscose from cuprammonium cellulose solution, which is stable over long periods, particularly in the absence of air. A fresh viscose can

* *Zellulosechemie*, 7, 17 (1926).

† In this connection see also the extremely interesting work of Bergmann, *Ber.*, 59, 2773 (1926).

‡ H. Pringsheim, J. Leibowitz, A. Schreiber and E. Kasten (*Annalen*, 448, 163 (1926), and also K. Hess, W. Weltzien and E. Messmer (*Annalen*, 435, 1 (1924)), conclude that the cellulose molecule consists of the unit $C_6H_{10}O_5$; see also G. Kita, J. Sakurada and T. Nakashima, *Zellulosechemie*, 8, 107 (1927). My views on the aggregation of micellae do not in themselves contradict this hypothesis.

§ A. Zart and L. Mönkemeyer, *Chemikerzeitung*, 48, 192 (1924).

be kept at the ordinary temperature for 8 to 10 days, at most, without coagulating. The temperature influences the process considerably, and at the boiling point coagulation occurs in a few minutes.

If too many xanthate groups have separated during the ripening process, the residual complex is ultimately no longer soluble and is precipitated as a gelatinous mass. Sodium hydroxide solution has a peptonizing effect on the xanthate. Coagulation does not occur so rapidly in dispersing agents containing more sodium hydroxide than in those containing less or even in pure water. There is an optimum amount of alkali which depends on the cellulose contents.

Many proposals have been made for additions to viscose at one stage or another of its preparation, or to the finished product. They are supposed to prevent the oxidation of the cellulose in viscose or the adhesion of the finished fibres. Sometimes they are added for other purposes. Probably none of these proposals are of any practical importance.

Proposals for freeing viscose from impurities, more particularly from trithiocarbonate, before the actual spinning process, by precipitation and re-solution were formerly made. They were, however, never used in practice, as the precipitation of viscose and the washing of the precipitated product are accompanied by exceptional difficulties. A real purification can scarcely be carried out, and does not appear to be necessary, as if the xanthation process is properly conducted no very great excess of trithiocarbonate is formed, under which conditions it is not harmful. When the trithiocarbonate is decomposed, hydrogen sulphide and carbon disulphide are liberated, whilst the xanthate, which is a dithiocarbonic ester, forms carbon disulphide only on decomposition.

The recovery of this carbon disulphide is not profitable in view of its low cost and the small quantities which are involved, but care must be taken for the removal of the carbon disulphide and the hydrogen sulphide during the spinning process by a good draught, in order to avoid discomfort and illness of the workers.

Apart from the manufacture of artificial silk and other

artificial fibres, viscose is used for the manufacture of so-called "artificial horsehair" (individual fibres of about the thickness of natural horsehair), and also for the production of small ribbons, which are endless single fibres of a few millimetres in width. Viscose is also used for the manufacture of films, similar to those produced from cellulose nitrate on pouring machines. The viscose is extruded from a slot of suitable size on to a drum rotating in a precipitating bath or on to an endless band, and is continuously precipitated and washed, desulphurized and dried. These films are, of course, sensitive to a certain degree to the action of water, in the same manner as artificial silk, and cannot, therefore, be used for photographic purposes.

Spinning Baths. After having been ripened, the viscose is once more filtered, and either pumped or blown by compressed air into the spinning tanks. From the spinning tanks it is passed through further filters to the spinning machines, in which it is converted into artificial silk fibres, the wet spinning process being exclusively used. Spinning baths usually consist of solutions of mineral acids—usually sulphuric acid—to which sodium sulphate is added in varying proportions, according to the well-known Müller patent (German patent 187,947) and that of the Vereinigten Glanzstoffabriken (German patent 287,955). According to the latter patent, almost saturated solutions of sodium sulphate in dilute sulphuric acid are used. This process was of exceptional importance in the development of the artificial silk industry.*

Within the range of acid concentrations in question, the temperature coefficient of the solubility of sodium sulphate is very small,† which is of special importance, as these spinning baths are usually used at fairly high temperatures of 40° to 50° C. It is only at lower temperatures, below 20° C., that the solubility of hydrated sodium sulphate becomes smaller, causing practical disadvantages, and such temperatures are, therefore, avoided in practice.

On the spinning bobbins the concentration of sulphate

* See V. Hottenroth, *Artificial Silk* (Sir Isaac Pitman & Sons, Ltd., London).

† O. Faust and P. Esselmann, *Zts. f. anorg. Chem.*, 157, 290 (1926).

becomes very high, in consequence of the neutralization of the alkali of the viscose by the entrained acid ; consequently, when using this spinning bath (which is employed almost everywhere) a secondary bath is generally used, which is already mentioned in the patent specification. Provision for such a bath is indicated, for example, in Fig. 28. This bath is supplied with dilute sulphuric acid, which dissolves sodium sulphate more easily than water, and the thread which has just been wound on to the bobbin is freed from a considerable quantity of sulphate on rotating in this acid, so that the sulphate does not crystallize out at a later stage. This is important as the sharp crystals of this salt would easily damage the soft thread. The liquid in the upper bath is circulated in a separate system, similarly to the spinning bath. This preliminary washing of the bobbins with dilute acid greatly assists the final washing process, as bobbins containing too much sodium sulphate swell greatly when first introduced into water, and therefore initially offer very great resistance to the passage of the washing water. A large number of patents and proposals deal with the preparation of spinning baths, and are all referred to in Süvern's handbook,* which has already been referred to ; none of these patents or proposals have, however, so far attained anything approaching the practical importance of the two patents above mentioned.

The inventors of viscose, Cross and Bevan, advised the use of a concentrated solution of an ammonium salt for precipitating that substance. Such precipitation baths are quite practical, and are still occasionally used to-day, usually at high temperatures in order to assist coagulation. The ammonium salts are decomposed with separation of ammonia, and thus remove from the xanthate the alkali which is necessary in order to dissolve it. Coagulation of the xanthate therefore occurs, and it is decomposed after a short interval at a fairly high temperature in these salt solutions, with reformation of cellulose hydrate.

Baths containing concentrated salt solutions, the above-mentioned Müller baths and those containing ammonium

* Süvern, *Die kunstliche Seide*, 5th Edition (Berlin, J. Springer), 440-534.

salts, all exercise a strong osmotic action on the fibre. When the spinning solution is discharged from the nozzle, the surface of the extruded stream of liquid is first coagulated to form a tubular structure, and this tube acts as a semi-permeable membrane during the osmotic process. The greater the concentration of salt and the higher the temperature of the precipitation bath, the greater is the osmotic action, which has a considerable influence on the cross-section of the finished fibre. Under the action of osmosis, water is withdrawn from the interior of the partially coagulated thread, which shrinks and thus acquires a more or less irregular cross-section.*

The attempts to use pure sulphuric acid as a precipitating bath have never ceased, and quite satisfactory results have occasionally been obtained with that acid (German patent 389,394). Whilst in former years bisulphate was available in sufficient quantity for the preparation of spinning baths, and was the cheapest material available, being a by-product of nitric acid manufacture, this is now no longer the case in consequence of the revolution in the manufacture of sulphuric acid; consequently, the use of cheap sulphuric acid as a precipitating agent is particularly desirable. It is true that during the spinning process sulphate is always formed in consequence of the neutralization of sodium hydroxide, and may, if required, be increased in amount by concentration of the waste acid. The used spinning bath is, in any case, not rejected, but is regenerated by suitable additions. A certain proportion of the spinning bath is naturally lost in the wash water. Apart from the osmotic action of baths containing acid and salt, the object aimed at to-day is usually to modify the exceptionally violent action of pure mineral acid, even at the ordinary temperature, by suitable additions. This aim has been attempted by the addition of organic acids and also of other organic compounds such as sugar, and so forth. Up to date, however, the Müller bath has maintained its position as the one which is used predominantly in the artificial silk industry. Apart from sodium sulphate, other salts, such as zinc salts,

* See also pages 23 to 26, and also the cross-sections by E. Bronnert shown in Figs. 335-336 of the Fourth Edition of Süvern's book, (1924).

may be added to the spinning bath. Other solvents have also been added, together with sodium sulphate, as the solubility of the latter is limited.

Exceptionally strong fibres are obtained by spinning viscose in sulphuric acid baths containing 55 per cent and more of H_2SO_4 , as proposed by L. Lilienfeld.* Lilienfeld prefers concentrations of 65 to 85 per cent of H_2SO_4 , which he adjusts according to the alkali contents of the viscose. Salts, such as ammonium sulphate, together with glucose and the like, may also be added to the spinning bath. These high concentrations of the acid, which were previously carefully avoided (those previously used being 5 per cent to 20 per cent H_2SO_4), obviously exercise a parchmentizing action on the fibre. The wet strength of "homogenized" fibres produced by this new process is considerably higher than that of all artificial silks hitherto known. In order to increase the elongation (extensibility),† the fibre may subsequently be treated with reagents which cause shrinkage, usually mercerizing agents, which can be applied simultaneously with the desulphurizing agents.

An entirely new method was introduced by German patent 430,358 of the Vereinigten Glanzstoffabriken, in which the addition to the spinning bath of aromatic sulphonic acids or of condensation products of these with formaldehyde is proposed; many other similar proposals have been made.

* British patents 264,161 and 261,352; Swiss patent 122,788.

† L. Lilienfeld, British patents 274,521, 274,690, and 281,352.

CHAPTER XIV

CONCLUSION

IN the first (German) edition of this book we were able to reproduce statistics published in *Die Seide* on the world's production of natural silk for the years 1914 and 1925, and of artificial silk for the years 1913 and 1925, which were as follows—

<i>Natural Silk</i>			<i>Artificial Silk</i>		
1914	.	22,100 tons	1913	.	11,500 tons
1925	.	30,465 ..	1925	.	70,000 ..

In the course of 12 years, the production of artificial silk has become six times as large, in spite of the Great War, and has overtaken the production of natural silk by a large amount, in spite of the increased production of the latter. According to the Annual Report of Snia Viscosa, the world's production in 1925 was 83,000 tons. According to an American estimate* the world's production in 1927 was 111,250 tons: even this figure is probably considerably under-estimated, and the quantity for 1928 may be estimated to be almost 50 per cent greater.†

According to the statements of the most important Italian company, the production in 1925 was distributed as follows between the various countries—

U.S.A.	.	.	.	.	25,000 tons
Italy‡	.	.	.	.	13,000 ..
Germany§	.	.	.	.	12,000 ..
England	.	.	.	.	11,000 ..
France	.	.	.	.	6,500 ..
Belgium	.	.	.	.	4,500 ..
Holland	.	.	.	.	3,000 ..
Switzerland	.	.	.	.	2,500 ..
Other countries	.	.	.	.	5,000 ..

* *Zts. f. angew. Chem.*, 40, 1347 (1927).

† See also *Die Seide*, 33, 71 (1928) where the production for 1927 is estimated to have been 120,000 tons.

‡ 70 per cent of which was due to the Snia Viscosa.

§ According to *Die Seide*, loc. cit., in 1927 Germany held the second and England the third place.

The statistics given by *Die Seide* differ somewhat from the above Italian figures, and according to *Die Seide* the percentages of the world's production were as follows—

U.S.A.	.	.	.	.	.	30 per cent
Germany	.	.	.	.	.	15 „
England	.	.	.	.	.	14 „
Italy	.	.	.	.	.	14 „
France	.	.	.	.	.	8 „
Belgium	.	.	.	.	.	6 „
Holland	.	.	.	.	.	5 „
Switzerland	.	.	.	.	.	3 „
Other countries	.	.	.	.	.	5 „

According to statistics communicated by the Ersten Österreichischen Glanzstoffabriken in St. Polten to the *Kunstseide*, 9, 538 (1927), the consumption of artificial silk per head of the population of the various countries is as follows—

Switzerland	.	.	.	.	.	516 gm.
England	.	.	.	.	.	315 „
Belgium	.	.	.	.	.	268 „
U.S.A.	.	.	.	.	.	250 „
France	.	.	.	.	.	210 „
Germany	.	.	.	.	.	211 „
Italy	.	.	.	.	.	149 „
Holland	.	.	.	.	.	146 „
Austria	.	.	.	.	.	143 „

The Swiss consumption may be partly due to purchases by visitors.

According to the artificial silk journal *Rayon*, Vol. 4, Part 5, p. 13 (1927), the figures are as follows for the under-mentioned four countries—

England	.	.	.	.	.	360 gm.
France	.	.	.	.	.	260 „
Germany	.	.	.	.	.	190 „
Italy	.	.	.	.	.	150 „

Although the data obtained from these various sources do not completely coincide, they show quite clearly that the consumption of artificial silk per head in most countries is still relatively small, and therefore capable of very great

increase. This is obvious from the following figures which show the percentage utilization of fibres for clothing—

Cotton	80	per cent.
Wool	17.5	„
Artificial silk	1.65	„
Silk	about 0.7	„
Other materials	0.1	„

According to these figures, artificial silk is still used as a luxury article, similarly to natural silk, and the object which it is most desirable to achieve appears to be a widely extended replacement of cotton by artificial silk, an object which is more definitely realized by the staple fibre industry, and which only seems possible to-day by the aid of the viscose process, as the other processes are excluded from this possibility if only for the reason that they use cotton as a raw material.

In spite of the enormous increase in the world's production, the prospects of the artificial silk industry may be described as very good in view of the above figures, and this will particularly be the case if the attempts further to improve and vary the properties of artificial silk are successful, so that it may be used for purposes for which it is at present unsuitable. Valuable foundations for the attainment of such aims are already available. The increase of the tensile strength when wet is important in this connection, and I have suggested a possible method of solving this problem. The present annual world production of wool is 1.2 million tons, and that of cotton 5 million tons. It is an interesting fact that the quantity of artificial silk used in Germany has already attained 20 per cent of the amount of wool used in that country. In spite of their large production, North America and Germany are still importing countries. The German imports come mainly from Italy, which is followed by Holland, Belgium and Switzerland. The Dutch exports to Germany, in particular, have increased greatly.

A necessary condition for the enormous development of the artificial silk industry, which has just been indicated, was the development of a sound and far-sighted industrial policy, such as was reported in the daily Press during the past year.

The *Deutsche Allgemeine Zeitung* reported in No. 445/446 of their Home Edition of the 24th September, 1927, the formation of an Association (Gesamtverband) of the German artificial silk industry. This has absorbed the individual associations which previously existed, and now controls the production of viscose, cuprammonium and acetate silk. The purpose of the association is the promotion of the joint economic interests of the German artificial silk and staple fibre industry.

The same journal reports further on the 25th September, 1927, in No. 447/448, on the amalgamation of the international artificial silk industry which has now been completed by the inclusion of the French artificial silk groups, which were already united under the Comptoir des Textiles Artificiels, in the Glanzstoff-Courtaulds—Snia-Viscosa group. The amalgamation was mainly concerned with agreements regarding production and prices.

The German artificial silk industry has found it possible, on the basis of its internationally recognized technical experience and its inherent economic power, to maintain and expand the position which it occupied before the War, and its former influence, in spite of the powerful development of this industry in other countries during and since the War.

BIBLIOGRAPHY

B. MARGOSCHES, *Die Viskose* (Leipzig, 1906).—E. Bronnert, *Emploi de la cellulose pour la fabrication de fils brillants. imitant la soie* (Mülhausen, 1909).—Joseph Foltzer, *La soie artificielle et sa fabrication* (Cornimont (Vosges); Imprimerie Ch. Girompaire), 2nd Ed. (1909), 144 pp.—Dr. Franz Becker, *Die Kunstseide* (Halle, 1912, Wilhelm Knapp), 368 pp.—Dr. Valentin Hottenroth, *Die Kunstseide* (Leipzig, 1926, S. Hirzel), 492 pp.—Prof. Dr. Franz Reinthaler, *Die Kunstseide* (Berlin, 1926, Jul. Springer), 165 pp.—A. Chaplet, *Les Soies Artificielles*, 2nd Ed. (Paris, 1926, Gauthier-Villars & Cie.), 256 pp.—Joseph Foltzer, *Artificial Silk and its Manufacture*, translated by T. Woodhouse (London, 1926, Sir I. Pitman & Sons, Ltd.), 255 pp.—*Zusammenstellung der Patentliteratur über künstliche Seide*, Geh. Rat Dr. K. Süvern, 5th Ed. (Berlin, 1926, Jul. Springer), 1108 pp; "Patentzusammenstellung über Viskoseseide usw. aus den letzten 10 Jahren." Dr. Bayer, *Melliands Textilberichte*, 8, 264, 876 (1927). "Bearbeitung der das Kunstseide- und Textilgebiet betreffenden Patente." G h. Rat Prof. Dr. A. Lehne, (Ziensen, Wittenberg).—Johann Eggert, *Die Herstellung und Verarbeitung der Viskose unter besonderer Berücksichtigung der Kunstseidenfabrikation* (Berlin, 1926, Jul. Springer), 92 pp.—R. O. Herzog, *Technologie der Textilfasern 7, Kunstseide* (Berlin, 1927, Jul. Springer).—Charles E. Mullin, *Acetate Silk and Its Dyes* (New York, van Nostrand, 1927), 490 pp.—K. Kretschmer, *Die Schlichterei in ihrem ganzen Umfange*, 2nd Ed. (A. Ziensen, Wittenberg, Bez. Halle, 1928).—V. Hottenroth, *Artificial Silk*, translated by E. Fyleman (Sir I. Pitman & Sons, Ltd).

ANALYSIS

Prof. Dr. Alois Herzog, *Die mikroskopische Untersuchung der Seide mit besonderer Berücksichtigung der Erzeugnisse der Kunstseidenindustrie* (Berlin, 1924, Jul. Springer), 197 pp.—H. Jentgen, *Laboratoriumsbuch für die Kunstseide- und Ersatzfaserstoff-industrie* (Halle, 1923, Wilh. Knapp), 104 pp.: Schwalbe-Sieber, *Die chemische Betriebskontrolle in der Zellstoff- und Papierindustrie*, 2nd Ed. (Berlin, Jul. Springer), 374 pp. Prof. Dr. Paul Heermann, *Mechanisch- und physikalisch-technische Textiluntersuchungen*, 2nd Ed. (Berlin, 1923, Jul. Springer), 270 pp.—Prof. Dr. Paul Heermann, *Technologie der Textilveredlung*, 2nd Ed. (Berlin, 1926, Jul. Springer), 656 pp.

WORKS OF WIDER INTEREST DEALING PARTLY WITH CELLULOSE AND ARTIFICIAL SILKS

C. G. Schwalbe, *Chemie der Zellulose* (Berlin, Gebr. Borntraeger).—E. Heuser, *Lehrbuch der Zellulosechemie*, 3rd Ed., 278 pp. (Berlin, 1928, Gebr. Borntraeger).—P. Karrer, *Polymere Kohlehydrate* (Leipzig, 1926, Akad. Verlagsges.).—H. Pringsheim, *Polysaccharide*, 2nd Ed. (Berlin, 1923, Jul. Springer).—Cross and Bevan, *Researches on Cellulose*,

I-IV, 1895-1900, 1900-1905, 1905-1910 : Cross and Dorée, 1910-1921 (London, Longmans, Green & Co.).—A. W. Schorger, *The Chemistry of Cellulose and Wood* (McGraw-Hill Book Co., Inc., New York and London), 596 pp., 1926.—E. C. Worden, *Technology of Cellulose Esters* (in 10 vols., so far published, Vol. I in 5 parts), 3709 pp. (Eschenbach Printing Co., Easton, Pa., 1921).

ECONOMIC AND COMMERCIAL

Dr. Martin Hölken, *Die Kunstseide auf dem Weltmarkt* (Berlin, 1926, Jul. Springer), 82 pp.—C. Königsberger, *Die deutsche Kunstseiden- und Kunstfaserindustrie in den Kriegs- und Nachkriegsjahren*, 172 pp. (Walter de Gruyter & Co., Berlin and Leipzig, 1925).—*Die Kunstseide*, 8, 346 (1926) (Berlin-Lichterfelde H. Jentgen).—C. Claessen, 25 Jahre Kunstseide, Jubiläumsheft, *Papierfabrikant*, 102 (1927).—*Die Kunstseidenindustrie* (H. Jentgen Berlin-Lichterfelde).—*The Artificial Silk Handbook* (J. Heywood, Ltd., Manchester), 3rd ed. (1928), 142 pp., contains statistics, suppliers of plant, and much generally useful information, especially for users of artificial silk.

GERMAN PERIODICALS (SCIENTIFIC)

Die Kunstseide. Die Seide. Kunststoffe. Metliands Textilberichte. Zellulosechemie. Zeitschrift für angewandte Chemie. Chemiker-Zeitung. Leipziger Monatschrift für Textilindustrie.

GERMAN PERIODICALS (ECONOMIC)

Die chemische Industrie (Berlin, Verlag Chemie). *Die Kunstseide* (Berlin-Lichterfelde, H. Jentgen). *Die Seide* (Krefeld).—*Handbuch der Internationalen Kunstseideindustrie von Curt und Jut. Mossner* (Finanzverlag, Berlin (1928)), 710 pp.

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